Revised as of January 2009

1/6/03 Physics 4523

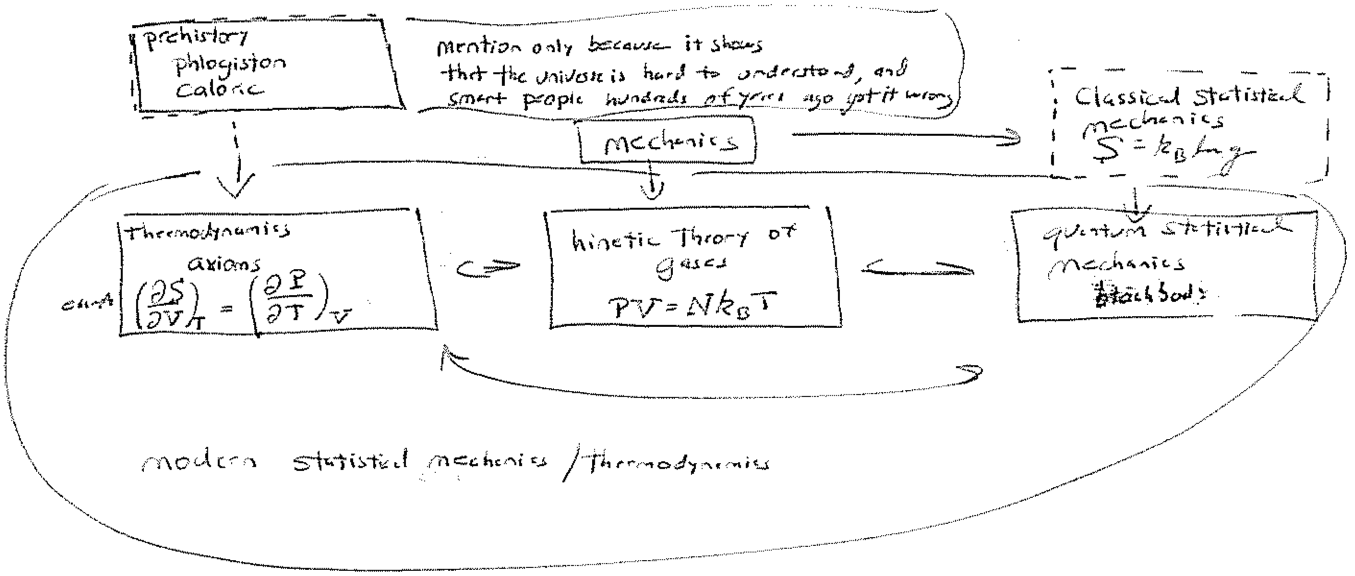
today: What is this course?
What is temperature?
Start counting microstates.

W, F: counting microstates

<u>This course</u>

The problem: how to extract information from far too many degrees of freedom.

Historical currents (course not historical – much too hard!)



why: $\nexists$ "classical" statistical mechanics ?

READ GOODSTEIN

Administrative : Hand out syllabus + HW

policies (in syllabus): HW
cheating
PREREQ.
books – library

Roll call

Replace too many degrees of freedom with a small number of measurable (or inferable) **State variables**. For example, for a gas in a box, these might be

pressure	P
volume	V
temperature	T
internal energy	U
# molecules	N
entropy	S

} not all independent

Organize

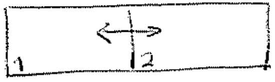
explain

extensive	**intensive**
N	T
V	P
S	color ?
mass	
energy	
momentum	

neither

- $\sqrt{\text{mass}}$
- speed
- time

Equilibrium & connection between intensive quantity and something conserved that they can exchange:



intensive quantity same in 1 & 2	if	two systems can exchange	how (example)
pressure		volume	piston
chemical potential		particles	hole in container; electrical
temperature		energy	thin rigid wall (thermally & conductive)

Steady state: no $\overset{\text{on ave.,}}{}$ change in any state variables.

Equilibrium: Steady state AND no $\overset{\text{ave.}}{}$ net flow of exchangeable quantities with ANY other systems (individually, not just collectively)

What is temperature? A (p)review (mostly a review of Physics I, but we'll do all of this more carefully later).

1. "That scalar $\overset{\text{intensive}}{\wedge}$ quantity shared by two objects in equilibrium if they can exchange energy." – not unique, doesn't even tell about ordering

   so – 2nd law (special application): heat flows hotter ⇒ colder until equilibrium reached

   Still doesn't tell us how to measure it

   Combined w/ 1st law, eventually get to heat engines (below)

2. practical expansion-type thermometer

Gabriel Daniel Fahrenheit 18th c. prev. used alcohol – too big & inaccurate

0°F = freezing of salt water (coldest liquid he could get)

100°F = body temp.

So Fahrenheit was intended to be a centigrade scale

3. From kinetic theory of gases, we find for $\boxed{\text{ideal gas}}$ (explain) that

$$PV = N\cdot\frac{2}{3}\left\langle \tfrac{1}{2}mv^2\right\rangle_{\text{ave.}} \quad \text{regardless of gas}$$

$$\underline{\text{Define}}\ \text{temperature}\ \ k_B T = \frac{2}{3}\left\langle \tfrac{1}{2}mv^2\right\rangle\ ;\ \text{Then}\ \boxed{PV = Nk_BT} \rightarrow \begin{array}{l}\text{gas}\\ \text{thermometer}\end{array}$$

NOTE: T ≥ 0

k_B: arbitrary constant to convert energy units into temperature units

K&K set $k_B \equiv 1$ to define $\tau = \frac{2}{3}\langle \frac{1}{2}mv^2\rangle = k_B T$

i.e., measure temperature in ergs

I'll usually keep the k_B in class.

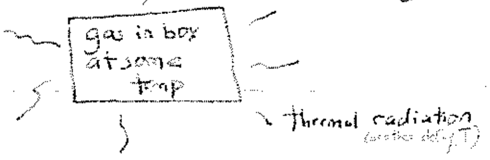
$$k_B \approx 1.38\cdot 10^{-16}\ \text{erg/K}$$

Subtlety: temperature is not exactly the same thing as kinetic energy. For example,

Observe –

$\longrightarrow$

v – fast but ≪ c



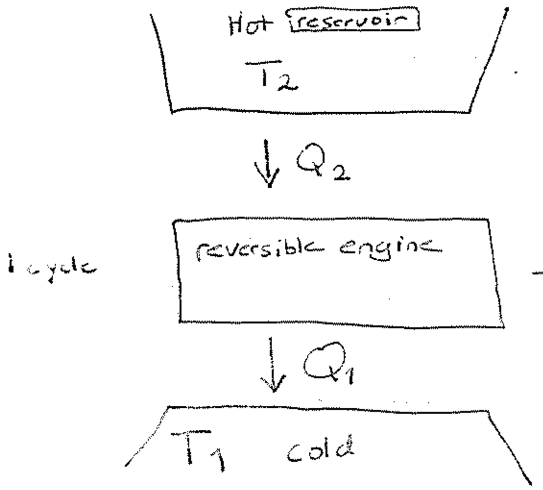
inadequacies of ideal gas:

- real gases interact
- wrong at low temp. even for ideal gas because of QM

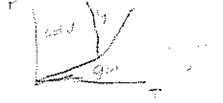
We do NOT add v to the rms velo. of the gas molecules in the box: $T' = T$. So the relevant K.E. is the "random part," not the center-of-mass motion.
(In fact, the temp. is Lorentz contracted, but we've kept $v \ll c$.)

1/5/03

4. Heat Engine



You found in Physics 1 that $\frac{Q_2}{Q_1} = \frac{T_2}{T_1}$: taking this as a definition gives a way of measuring temperature
(Carry around a reference reservoir at T_1; measure Q_1 & Q_2 to get T_2)
e.g. triple point of H_2O



1/6/03

5. Stat. Mech. : to develop in detail this week and next

macrostate : $P, V, T, \underset{\sim}{U}, \ldots$ internal energy — not all independent, small #

Assume $U^{\text{or } V}$ determines all the rest
(e.g., ideal gas in rigid box)

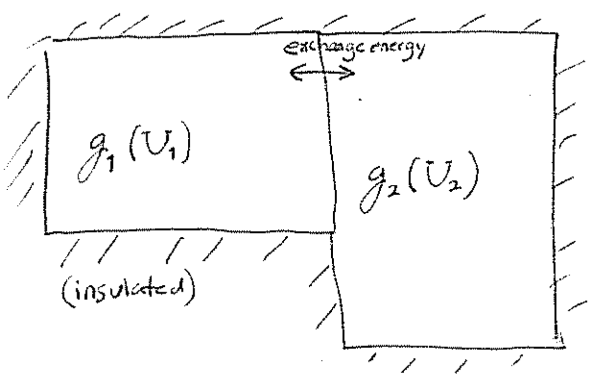
microstate : $\vec{x}_1, \vec{p}_1, \vec{x}_2, \vec{p}_2, \cdots, \vec{x}_{10^{23}}, \vec{p}_{10^{23}}$ large #

Many microstates per macrostate - let $g(U)$ be "number"* of ways to pick $\{x_i, p_i\}$ consistent with U.

[* Boltzmann's suicide

ergodic hypothesis : All microstates consistent w/ a given macrostate are equally likely ; system goes through "all" of them on a time scale short compared to the expt. ("all" = arbitrarily close, or close enough, in phase space).

Two systems in thermal equilibrium — can exchange energy but not volume or particles. T will be "that thing" which is the same @ equilibrium



total $U = U_1 + U_2$ fixed

["microcanonical ensemble" to explain later]

$$\text{total \# configs } g(U_1, U_2) = g_1(U_1)\,g_2(U_2) = g_1(U_1)\,g_2(U-U_1) \equiv g(U_1)$$

Ansatz : if all <u>microstates</u> are equally likely, then the equilibrium <u>macrostate</u> is the one corresponding to the largest number of <u>microstates</u>.

explain not'n

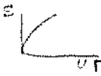
$$\text{set } 0 = \left(\frac{\partial g(U_1)}{\partial U_1}\right)_N = g_1'(U_1)\,g_2(U-U_1) - g_1(U_1)\,g_2'(U-U_1)$$

$$\text{i.e., } \underbrace{\frac{g_1'}{g_1}}_{\text{property of \#1 alone}} = \underbrace{\frac{g_2'}{g_2}}_{\text{property of \#2 alone}}$$

looks like log deriv.

$$\text{So } T = \overset{\sim\text{ some fcn.}}{f}(g'/g) = f\left(\frac{\partial S}{\partial U}\right)_N$$

where $S \equiv k_B \ln g$



Argue that $g'/g \sim \infty$ when $U=0$ ([illegible])

will improve later

Intuitively, hot ⇒ g big
cold ⇒ g small ,

so we define $f(x) = 1/x$; i.e., $\boxed{T \equiv \left(\frac{\partial U}{\partial S}\right)_N}$

Start on counting microstates

We'll follow K&K considering a very simple system, the binary-spin model. ("Ising" usually reserved for interacting spins - Ours will interact only with a magnetic field, not with each other.)

↑ ↑ ↓ ↑ ↑ ↓ ↓

Each classical spin (moment) ↑ +1 or ↓ −1   will be useful later when we turn on mag. fld.

1) very simple - exactly solvable

2) other similar systems aren't so easy (HW)

3) generic features of $g(U)$ are good for large # of spins

energy $U = -\mu m B$

	config	dimensionless moment m	$g(m)$	probability **IF B=0**
one spin	↑	+1	1	50%
two states	↓	−1	1	50%
			$2 = 2^1$	
two spins	$\uparrow_1 \uparrow_2$	+2	1	25%
four states	$\uparrow_1 \downarrow_2$	0	2	50%
	$\downarrow_1 \uparrow_2$	0		
	$\downarrow_1 \downarrow_2$	−2	1	25%
			$4 = 2^2$	
three spins	$\uparrow_1 \uparrow_2 \uparrow_3$	3	$g(3) = 1$	12.5%
eight states	↑↑↓	1	$g(1) = 3$	37.5%
	↑↓↑			
	↓↑↑			
	↓↓↑	−1	$g(-1) = 3$	37.5%
	↓↑↓			
	↑↓↓			
	↓↓↓	−3	$g(-3) = 1$	12.5%
			$8 = 2^3$	

Assuming no mag. fld., all 8 STATES are equally likely. However, it is 3x more likely that $m_{tot} = +1$ than $m_{tot} = +3$.

1/8/03

Monday : intro ; 4 definitions of T

Today: 5^{th} def. of T

counting μstates

Fri. : sharpness of distribution

(pp 4-6 left-over)

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* Say something about turning on mag. fld. At T=0, all in ground state ↑↑↑. However, we'll see that for $B \neq 0$, $T > 0$, there's some probability for each state.

For general N :

Let $N_\uparrow = \#$ up spins , $N_\downarrow = \#$ down spins $= N - N_\uparrow$

How many ways are there to have $N_\uparrow$ up & $N_\downarrow$ down?

answer: $$g(N; N_\uparrow) = \frac{N!}{N_\uparrow!\ N_\downarrow!} = \frac{N!}{N_\uparrow!\,(N-N_\uparrow)!} \equiv \binom{N}{N_\uparrow} = \binom{N}{N_\downarrow}$$ read "N choose $N_\uparrow$"

argument: N choices of where to put 1^{st} up spin

N-1 " " " " " 2^{nd} " " , because one slot's taken

N-2 " " " " " 3^{rd} " " ,

⋮

$N - N_\uparrow + 1$ " " " last " "

SO FAR we have $$g \propto N\,(N-1)\,(N-2) \cdot \ldots \cdot (N - N_\uparrow + 1)$$

$$= \frac{N\,(N-1)\,(N-2)\ \ldots\ (N-N_\uparrow+1)(N-N_\uparrow)(N-N_\uparrow-1) \cdots 3\cdot 2\cdot 1}{(N-N_\uparrow)\,(N-N_\uparrow-1) \cdots 3\cdot 2\cdot 1}$$

$$= \frac{N!}{(N-N_\uparrow)!}$$. However, we've overcounted, because

I don't care which was the first up spin, which the second, etc.

It overcounts by a factor of $N_\uparrow!$ → answer above

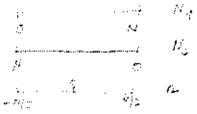
⑧

Sometimes it's convenient to define

$$s = \frac{N_\uparrow - N_\downarrow}{2}$$

$2s$ called "spin excess" - for example, if I have 40 spins, and 22 are up, $s = \frac{22-18}{2} = \frac{4}{2} = 2 = N_\uparrow - \frac{N}{2}$

$$N_\uparrow = N/2 + s$$
$$N_\downarrow = N/2 - s$$



so $g(N,s) = g(N; \frac{N}{2}+s) = \dfrac{N!}{(\frac{N}{2}+s)!\,(\frac{N}{2}-s)!}$

1/9/04

$g(N; N_\uparrow)$ called "binomial coef." because in formal product

$$(\uparrow + \downarrow)^N = (\uparrow + \downarrow)(\uparrow + \downarrow)\cdots(\uparrow + \downarrow) = \uparrow\uparrow\uparrow\cdots\uparrow\uparrow + \uparrow\uparrow\uparrow\cdots\uparrow\downarrow + \cdots$$

if we collect terms by total numbers of up & down, we have

$$(\uparrow + \downarrow)^N = \sum_{N_\uparrow = 0}^{N} \binom{N}{N_\uparrow} \uparrow^{N_\uparrow} \downarrow^{(N-N_\uparrow)}$$

Pascal's triangle to calculate binomial coef.:

N = 0	1
1	1 1
2	1 2 1
3	1 3 3 1
4	1 4 6 4 1
	⋮

7/8/03

Sharpness of coin flips (I don't mean what is chance it will land on edge)

Assume coin unbiased.

Most likely outcome is 50% heads, 50% tails, but I might not get <u>exactly</u> 50-50.

Example: 4 coins

0 heads	$1/16$	= 6.25%
1 head	$4/16$	= 25%
2	$6/16$	= 37.5
3		25%
4		6.25%

only a 37.5% chance of <u>exactly</u> 50%-50%, but an 87.5% chance it's <u>between</u> 25%-75% & 75-25.

How about 1000 coins?

According to my calc.:

exactly 50%-50% (i.e., 500 heads, 500 tails) : only 2.5% chance

but chance it's between 25%-75% (250 heads, 750 tails)

and 75%-25% (750 heads, 250 tails)

is about $1-4\cdot10^{-59}$, i.e.,

$$\underset{58}{\underset{\longleftrightarrow}{99.9999\cdots9996}}$$

Show histograms unscaled & scaled — comment on sharpness

Next: continuum approximation

1/10/03 Wed.: counting μstates; binomial expansion

today: binomial → continuum approximation → Gaussian

averages

Monday: Canonical ensemble

SET OFFICE HOURS

left-over page (9)

$$g(N,s) = \frac{N!}{(\frac{N}{2}+s)!\,(\frac{N}{2}-s)!}$$

— graphs → need for continuum approx'n

first step in algebra — tame big numbers by taking log:

$$\ln[g(N,s)] = \ln(N!) - \ln[(\tfrac{N}{2}+s)!] - \ln[(\tfrac{N}{2}-s)!]$$

Two approximations:

1) Stirling series $\ln(n!) \sim n\ln n - n + \frac{1}{2}\ln n + \frac{1}{2}\ln(2\pi) + \frac{1}{12n} + \cdots$
2) $s/N \ll 1$: justified by what we've seen so far: away from center ($s=0$), $\frac{g(N,s)}{2^N} \ll 1$.

empirical test of Stirling:

n	$\ln(n!)$	$n\ln n - n$	$n\ln n - n + \frac{1}{2}\ln n + \frac{1}{2}\ln(2\pi)$
3	1.7918	0.2958	1.7641
10	15.104	13.026	15.096
50	148.48	145.60	148.48
100	363.74	360.52	363.74

Contrast Taylor & asymptotic series:

	Taylor (in x)	asymptotic (in $\frac{1}{n}$)
for fixed # terms better as x or $\frac{1}{n} \to 0$	✓	✓
for fixed x or $\frac{1}{n}$, better with more terms	✓	✗

derivation of Stirling

1. K&K app. A — tedious but elementary
2. Bender & Orszag Adv. Math. Methods for Sci. & Eng. 3 methods

$$\ln[g(N,s)] = N\ln N - \cancel{N} + \tfrac{1}{2}\ln N - \left(\tfrac{N}{2}+s+\tfrac{1}{2}\right)\ln\left[\tfrac{N}{2}+s\right] + \cancel{\tfrac{N}{2}} + \cancel{s}$$
$$- \left(\tfrac{N}{2}-s+\tfrac{1}{2}\right)\ln\left[\tfrac{N}{2}-s\right] + \cancel{\tfrac{N}{2}} - \cancel{s} - \tfrac{1}{2}\ln(2\pi)$$

write $\ln\left(\frac{N}{2} \pm s\right) = \ln\left(\frac{N}{2}[1 \pm \epsilon]\right)$ where $\epsilon \equiv \frac{2s}{N}$ assumed $\ll 1$

$= \ln N - \ln 2 + \ln(1 \pm \epsilon)$

<u>TAYLOR</u> $\approx \ln N - \ln 2 \pm \epsilon - \frac{1}{2}\epsilon^2 \pm \frac{1}{3}\epsilon^3 - \ldots$ keep ϵ^3 term just to estimate our error at the end

$$\ln[g(N,s)] \approx \left(N+\tfrac{1}{2}\right)\ln N - \left(\tfrac{N+1}{2}+s\right)\left(\ln N - \ln 2 + \epsilon - \tfrac{1}{2}\epsilon^2 + \tfrac{1}{3}\epsilon^3\right)$$
$$- \left(\tfrac{N+1}{2}-s\right)\left(\ln N - \ln 2 - \epsilon - \tfrac{1}{2}\epsilon^2 - \tfrac{1}{3}\epsilon^3\right) - \tfrac{1}{2}\ln(2\pi)$$

$$= \left(N+\tfrac{1}{2}\right)\ln N - (N+1)\ln N + (N+1)\ln 2 + \tfrac{1}{2}(N+1)\epsilon^2 - 2\epsilon s - \tfrac{2}{3}s\epsilon^3 - \tfrac{1}{2}\ln(2\pi)$$

$$= N\ln 2 + \tfrac{1}{2}\ln(2/(\pi N)) - 2s^2/N + 2(s/N)^2 - \mathcal{O}(s^4/N^3)$$

For $s=0$, $\ln[g(N,0)] \approx N\ln 2 + \frac{1}{2}\ln\left(\frac{2}{\pi N}\right) + \overbrace{\mathcal{O}(1/N)}^{\text{from Stirling}}$

take exponential: $\boxed{g(N,0) \approx 2^N\sqrt{\frac{2}{\pi N}}}$ $(\times e^{\sim/N})$

Generally,

$$g(N,s) \approx g(N,0)\exp\left[-2\frac{s^2}{N} + \underset{\substack{\uparrow \\ \text{very small}}}{2\left(\frac{s}{N}\right)^2} - \underset{\substack{\uparrow \\ \text{really truly small}}}{\mathcal{O}\left(\frac{s}{N}\right)^3}\right]$$

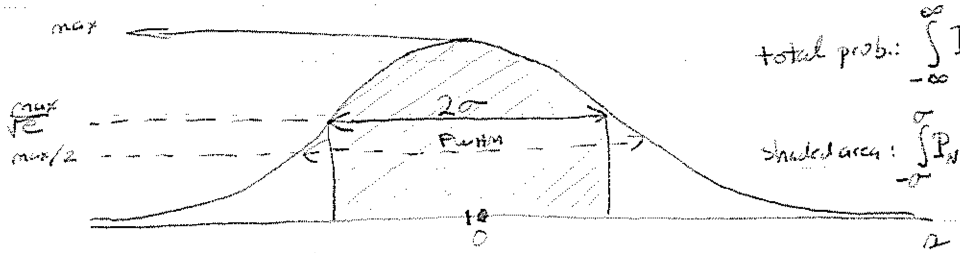
What's left is a Gaussian (normal, bell-shaped curve).

Recall we assume no mag. field.

$P_N($[illegible]$s) =$
probability $(N,s) = \dfrac{g(N,s)}{2^N} = \sqrt{\dfrac{2}{\pi N}}\,e^{-2s^2/N}$

Put in form of a normal distribution: $P_N(s) = \dfrac{1}{\sigma\sqrt{2\pi}}\,e^{-s^2/(2\sigma^2)}$

σ called standard deviation; here $\sigma = \frac{1}{2}\sqrt{N}$



total prob.: $\int_{-\infty}^{\infty} P_N(s)\,ds = 1$ note endpoints: originally ±N/ hardly diff ±∞

shaded area: $\int_{-\sigma}^{\sigma} P_N(s)\,ds = \mathrm{erf}\left(\frac{1}{\sqrt{2}}\right) \approx 0.6827$

So s PROBABLY lies between $-\sigma$ & $+$
ie, $\pm\frac{1}{2}\sqrt{N}$

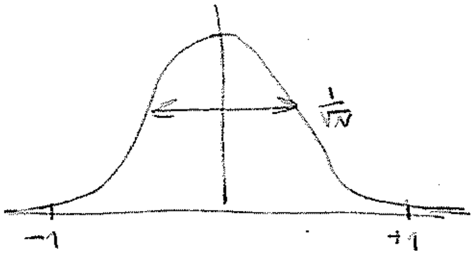
mention erf

⑫

Natural variable is not s but rather $x = s/N = \frac{1}{2}\frac{N_\uparrow - N_\downarrow}{N}$

(i.e., magnetization PER SPIN rather than total)

standard deviation $\sigma' = \frac{\sigma}{N} = \frac{1}{2\sqrt{N}}$



so 68% prob $\frac{s}{N}$ lies between $\pm \frac{1}{2\sqrt{N}}$
95% " " " " $\pm \frac{1}{\sqrt{N}}$
99.7% " " " " $\pm 3/(2\sqrt{N})$

1/10/03, [illegible]

Averages. If heads are worth +1 & tails −1, what is avg. coin toss?

$$\langle x \rangle = \frac{1}{2}\sum_{x \in \pm 1} x = 0$$

Now say coin is weighted so that prob(+1) = 55%, prob(−1) = 45%.

$$\langle x \rangle = \sum_{x \in \pm 1} x\, P(x) = -1 \cdot 0.45 + 1 \cdot 0.55 = \boxed{+0.1}$$

For a continuous prob. distrib'n, $P(x)\,dx$ means "prob. of events between x & $x+dx$."

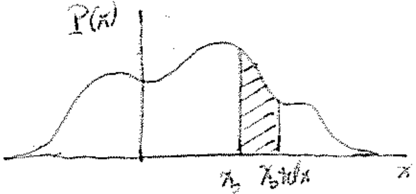
$$\langle x \rangle = \int x\, P(x)\, dx$$

For our binary-spin problem, $P(s) = \frac{1}{\sigma\sqrt{2\pi}} e^{-s^2/(2\sigma^2)}$, $\sigma = \frac{1}{2}\sqrt{N}$

avg. $\frac{1}{2}$spin excess, $\langle s \rangle = \frac{1}{\sigma\sqrt{2\pi}} \int_{-\infty}^{\infty} ds\, s\, e^{-s^2/(2\sigma^2)}$ integrand odd ⇒ $\underline{\underline{0}}$

avg. <u>square</u> ($\frac{1}{2}$spin excess) $\langle s^2 \rangle = \int_{-\infty}^{\infty} ds\, s^2\, P(s) = \sigma^2$ (see book)

General expectation values



$P(x)$ is prob. density of x.

shaded = prob. that $x_0 \leq x \leq x_0 + dx$

$$\int_{-\infty}^{\infty} P(x)\, dx = 1$$

$$\langle f(x) \rangle = \int_{-\infty}^{\infty} f(x)\, P(x)\, dx$$

1/13/03

last week: (p) review; counting μstates

today: averages
microcanonical ensemble

Wed.: the laws of thermodynamics

1. A few minutes on problems 2 & 3 from HW 1

It's sometimes easier to solve for the probability of something not happening.

Example: flipping four coins, what is the prob. of getting at least 1 head?

a) $P(1\text{ head}) + P(2) + P(3) + P(4) = \frac{4+6+4+1}{16} = \frac{15}{16}$

b) $1 - P(0\text{ heads}) = 1 - \frac{1}{16} = 15/16$

2. Finish p12 on averages

Microcanonical ensemble:

K&K: for each $\boxed{\text{accessible}}$ state of system, one copy of the system.

E.g., binary spin system, $N=4$, $\frac{1}{2}$spin excess $s=1$:

$\boxed{\cdot \mid \cdot \mid \cdot \mid \cdot}$ represented by 4 copies, one for each accessible state:

Now turn on B so energy diff. for ea. macrostate

$\boxed{\uparrow\downarrow\downarrow\downarrow}$ $\boxed{\downarrow\uparrow\downarrow\downarrow}$ $\boxed{\downarrow\downarrow\uparrow\downarrow}$ $\boxed{\downarrow\downarrow\downarrow\uparrow}$

"Accessible" in μcanonical ensemble means having same energy — implies furthermore some dynamical way of getting there in experimental time.

Examples of inaccessible: 1) glass — even though ~~quartz~~ fused silica could turn into quartz + heat & conserve energy, it can't get there from here even over millions (?) of years (nor diamond → graphite).

2) planetary system consisting of one star & one planet — many orbits have the same energy, but even over billions of years, there's no dynamical mechanism for going from one to ~~the~~ another, so stat. mech. not useful. (In this case,

there are other conserved quantities: angular momentum & the Laplace-Runge-Lenz vector).

Add a 3rd body, and motion could become either ergodic or chaotic.

3) QM exact stationary state — $\psi(x,t) = e^{-iEt/\hbar}\psi(x,0)$ stays the same forever (other than phase).
However, if ψ is a stationary state only of an approximate Hamiltonian, $\mathcal{H}_0$, with $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}'$, the perturbation $\mathcal{H}'$ may "ergodically" couple all stationary states of $\mathcal{H}_0$ with the same energy (quantum chaos — current research).

Ensemble average: $$\langle f \rangle = \frac{1}{\#\text{systems}} \sum_{\underset{(\text{state})}{s=1}}^{\#\text{systems}} f(s) = \frac{1}{g} \sum_{s=1}^{g} f(s)$$

Other ways to view μcanonical ensemble:

— ∞ many copies of the system, each started off in a different initial config. of the same energy (and other macroscopic vars.):
$$\langle f \rangle = \lim_{N\to\infty} \frac{1}{N} \sum_{\underset{(\text{system label})}{t=1}}^{N} f(s(t))$$
(each state eq. weighted)

— One system sampled at different times:
$$\langle f \rangle = \lim_{T\to\infty} \frac{1}{T} \int_0^T f(s(t))\,dt$$

According to the $\boxed{\text{ergodic hypothesis}}$, all of these give the same average.

Comment on notation: $\langle \cdot \rangle$ is ensemble average

In this chapter, avg. over μcanonical ensemble (U, N fixed).
In Ch. 3, avg. over canonical ensemble (T, N fixed).
Later, over grand canonical ensemble (T, μ fixed).
} will give equivalent results in equilibrium

Sometimes, we might need a quantum expectation value; if it's necessary to distinguish, we can write $\langle \cdot \rangle_{\text{thermal}}$ & $\langle \cdot \rangle_{\text{QM}}$.

Recall last week's derivation of Temp. —

skip

~~Before~~, I wrote $g(U_1) = g_1(U_1)\,g_2(U-U_1)$ for the most probable partition of energy between the two subsystems. At thermal equilibrium, this and a vanishingly small coterie are the only ~~[illegible]~~ partitions that matter. To be completely correct, $g = \sum_{U_1}' g(U_1) = \sum_{U_1}' g_1(U_1)\,g_2(U-U_1)$.

11/1/01
1/13/03

We found $\left(\frac{\partial S_1}{\partial U_1}\right)_N = \left(\frac{\partial S_2}{\partial U_2}\right)_N$ where $S_i \equiv k_B \ln g_i$.

Kittel give example of spin systems in thermal contact.

N_1, N_2 fixed; (½) spin excess $s_1 + s_2$ fixed, s_1 allowed to vary

($\mathcal{H}'$ has term flipping $\uparrow_{sys1} \downarrow_{sys2} \Longleftrightarrow \downarrow_{sys1} \uparrow_{sys2}$ – total spin conserved)

For $i = 1, 2$, $g_i(s_i) = g_i(0) e^{-2s_i^2/N_i}$, $g_i(0) = 2^{N_i}\sqrt{\frac{2}{\pi N_i}}$

Most likely config. satisfies

$$\frac{\partial}{\partial s_1}\left[g_1(s_1) g_2(s - s_1)\right] = 0$$

extremum occurs in same place for $g_1 g_2$ as for $\log(g_1 g_2)$, so

$$0 = \frac{\partial}{\partial s_1}\left[\ln g_1(s_1) + \ln g_2(s - s_1)\right] = \frac{\partial}{\partial s_1}\left[\ln g_1(0) - 2s_1^2/N_1 + \ln g_2(0) - 2(s - s_1)^2/N_2\right]$$

$$= -4s_1/N_1 + 4\,\underbrace{[s - s_1]}_{s_2}/N_2$$

so $\boxed{\frac{s_1}{N_1} = \frac{s_2}{N_2}}$ i.e., magnetization per spin equal in the two subsystems

Converting to energy (with magnetic field),

$$U = -\sum_{\text{spin } j} \mu m_j B$$

where $m_j = \pm 1$; $\sum_j m_j = N_\uparrow - N_\downarrow = 2s$, so

$s_1 = \sum_{\text{spin}} m_j$

$$U = -2\mu s B$$

Thus $\boxed{\frac{U_1}{N_1} = \frac{U_2}{N_2}}$ equal energy densities – this needn't be the case in general, however: systems 1 & 2 might not have the same magnetic moment μ, or they might not even be made of the same ~~stuff~~ Stuff – sys 1 might be an ideal gas and system 2 a hunk of iron. In general, however, it will be true that, at equilibrium,

$$\boxed{T_1 = T_2}$$

where $T_j = \left(\frac{\partial U_j}{\partial S_j}\right)_N$

Temperature for this example:

$$T_1 = \left(\frac{\partial U_1}{\partial S_1}\right)_{N_1} = \frac{1}{(\partial S_1/\partial U_1)_{N_1}} = \frac{1}{k_B \frac{\partial}{\partial U_1}\left[\ln g_1(0) - \frac{2}{N_1}\left(\frac{U_1}{2\mu B}\right)^2\right]}$$

use $s_1 = -\frac{U_1}{2\mu B}$

$$= \frac{1}{k_B\left(-\frac{U_1}{N_1\mu^2 B^2}\right)} = -\frac{N_1}{U_1}\frac{\mu^2 B^2}{k_B}$$

Similarly, $T_2 = -\frac{N_2}{U_2}\frac{\mu^2 B^2}{k_B} = T_1$.

Is this negative?

due to Lowest energy $\Leftrightarrow$ all spins ↑ $\Leftrightarrow s = N/2 \Leftrightarrow$ U <u>negative</u> so T pos

so configs w/ $s > 0$ have $T \geq 0$

configs w/ $s < 0$ have $T \leq 0$

1/15/03 Mon.: averages
ergodic hypothesis
microcanonical ensemble
~~to~~day: entropy
temperature
laws of thermodynamics
Fri: C.P. Snow
$e^{-E/(k_B T)}$
Z
discuss Homework 2

[Since I didn't specify <u>when</u> today HW would be due, it must be at midnight. In future, it will be due at start of class, when I shall hand out solutions.]

[finish p.15]

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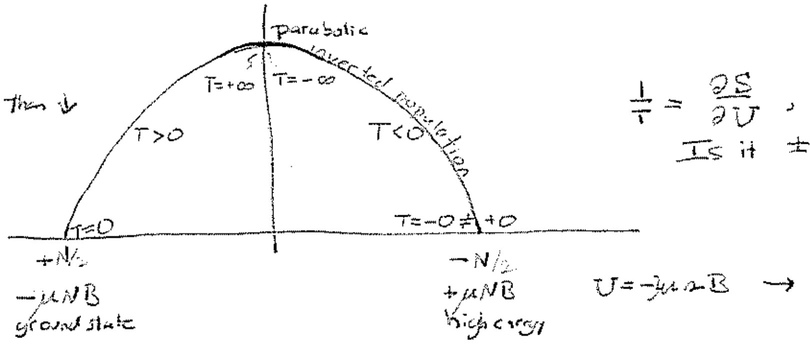
same thing graphically:

$$S + \text{const} = \text{const.} - 2k_B s^2/N$$

B ↑

↑ has lower energy than ↓



$\frac{1}{T} = \frac{\partial S}{\partial U}$, i.e., slope.

Is it $\pm\infty$ at ends or finite?

To get slope at edges, we cannot use Gaussian approx'n, since $|s|$ is not $\ll N$.

(Indeed, Gaussian continues parabola down forever.)

$$\text{Slope at } s = +\tfrac{N}{2} \approx \frac{\Delta S}{\Delta U} = \frac{S(s=\frac{N}{2}-1) - S(s=\frac{N}{2})}{U(s=\frac{N}{2}-1) - U(s=\frac{N}{2})} = \frac{k_B\left[\ln(g(N,\frac{N}{2}-1)) - \ln(g(N,\frac{N}{2}))\right]}{-\mu\left(\frac{N-2}{2}\right)B + \mu\frac{N}{2}B}$$

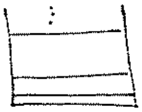
$$= \frac{k_B\left[\ln\binom{N}{N-1} - \ln\binom{N}{N}\right]}{\mu B} = \frac{k_B(\ln N - 0)}{\mu B} \xrightarrow[N\to\infty]{\lim} \infty$$

In limit of ∞ system, slope $\to +\infty$, so $\boxed{T=0}$ PENCIL IN PICTURE

For $s=0$, slope $=0$, so $\boxed{T=\infty}$

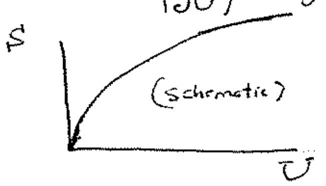
At this temperature, distribution is same as if there were no magnetic field (practical limit: $k_BT \gg \mu B$)

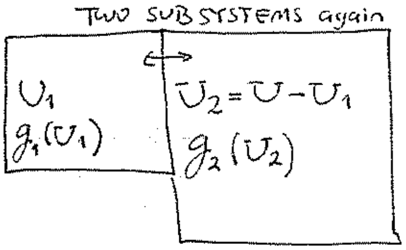
For $s<0$, slope <0, so $\boxed{T<0\ \ ?!}$ See appendix E & HW 2.2

Inverted population impossible in ~~[illegible]~~ system with arbitrarily high energy levels (e.g., particle in a box: )

Since $\left(\frac{\partial S}{\partial U}\right)^{-1}$ grows monotonically with U.

See HW 2.3





Say all energy starts out in subsys. 1: $U_1 = U$, $U_2 = 0$

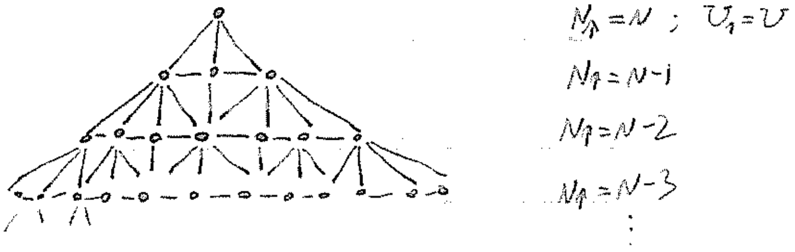
What will happen to the macrostates of the two subsystems?

. . .

Ok, so they've reached thermal equilibrium.

Is it $\boxed{\text{possible}}$ for them to return to original state? [Laws of physics are reversible.] Is it $\boxed{\text{likely}}$? All microstates consistent with total U are equally likely, but there are vastly fewer corresponding to $U_1 = U$ than to thermal equilibrium.

Schematic:
dots = microstates
rows = macrostates
lines = possible transitions in either direction



At each step, system can move to any connected point; it's possible but unlikely for it to evolve very far from equilibrium

1/15/03: Supreme Court decided earlier today that 95 years (beyond an author's death) is not "forever."

2^{nd} law of thermodynamics: entropy "never" decreases (monkey Hamlet)
In a small system, it rarely decreases; in a system with $\sim 10^{23}$ degrees of freedom, "never."

CARD GAME with students representing energy units (or equivalently gas molecules)

1/15/03

$\boxed{\text{Reversible}}$ processes: only infinitesimal deviations from equilibrium macrostate
irreversible: – dropping expensive Greek vase
$\boxed{\text{arrow of time}}$ – it appears that microscopic laws of physics don't provide it – only statistics

laws of thermodynamics:

0) If A & B are in thermal equilibrium, and B & C are, so are A & C. (Immediate consequence of $T = (\partial U / \partial S)_N$.)

1) Heat is a form of energy transfer, and energy is conserved.

IT'S A ZERO-SUM GAME (perpetual-motion machines of the first kind)

2) The entropy of the whole universe cannot decrease in time. equivalent: $\nexists$ heat engine whose sole effect in one cycle of operation is to convert heat from some source into mechanical work. (equivalence to be shown later in course).

YOU CAN'T WIN (Dilbert: perpetual-motion machine of the second kind?)

3) Entropy → constant (usually zero) monotonically as $T \to 0$

YOU CAN'T BREAK EVEN

⑲

1/17/03

Wed.: entropy, temperature

today: laws of thermo.

Boltzmann

Finish p18

C.P. Snow 1959 Rede lecture → Flanders + Swan (1964)

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background to problem 2.3

Classical harmonic oscillator: $\overset{\text{energy}}{U} = \dfrac{p^2}{2M} + \frac{1}{2}kx^2$

x = pos'n
p = momentum
M = mass
k = spring const.

QM: $\mathcal{H} = -\dfrac{\hbar^2}{2m}\dfrac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2$, $k = \omega^2 M$

solutions: $E_m = (m+\frac{1}{2})\hbar\omega, \quad m = 0, 1, 2, \ldots$

K+K simplify the algebra slightly by ignoring the 1/2 – for large N, it will not be significant in this problem

go over pp 24-25

N oscillators; number j can have any $m_j = 0, 1, 2, \cdots$
subject to $m_1 + m_2 + \cdots + m_N = n$ fixed

Mathematics: partitioning the integer n among N boxes

$g(\overset{N}{\cancel{M}}, \overset{n}{\cancel{m}})$ = # ways to portion $\overset{n}{\cancel{m}}$ among N boxes

"generating function" $\displaystyle\sum_{m=0}^{\infty} t^m = \frac{1}{1-t}$ for $0 < t < 1$ – t is just a formal device – will drop out @ end

proof:
let $A = \sum_{m=0}^{\infty} t^m$. Then $At = \sum_{m=1}^{\infty} t^m$, so $A - At = t^0 = 1$, or
$A = \frac{1}{1-t}$.

Consider a product of N of these sums:

$$\Big(\sum_{m_1} t^{m_1}\Big)\Big(\sum_{m_2} t^{m_2}\Big)\cdots\Big(\sum_{m_N} t^{m_N}\Big) = \left(\frac{1}{1-t}\right)^N$$

Expand l.h.s. → various powers of t. A term
$t^{m_1} t^{m_2} \cdots t^{m_N} = t^{\sum_j m_j} = t^n$

represents a config. in which osc. #j has energy E_{m_j}. We would like to fix $\sum_j m_j = n$. The number of terms contributing to t^n is $g(N, n)$, so

$$\left(\frac{1}{1-t}\right)^N = \sum_{m=0}^{\infty} g(N,m)\, t^m .$$

How can we pick out the one term we want? Take **n** derivatives w.r.t. t, then set $t \to 0$. Any term with t^m, $m > n$, will go to zero. Any term $m < n$ will be wiped out by the derivs. The term $m = n$ will have an unwanted $n!$ in front. So

$$g(N,n) = \lim_{t \to 0} \frac{1}{n!}\left(\frac{d}{dt}\right)^n \sum_{m=0}^{\infty} g(N,m)\, t^m$$

$$= \lim_{t \to 0} \frac{1}{n!}\left(\frac{d}{dt}\right)^n (1-t)^{-N}$$

$$= \frac{1}{n!} N(N+1)\ldots(N+n-1)$$

(Each deriv. has factors -1 from the exponent and -1 from $-t$)

$$= \frac{(N+n-1)!}{n!\,(N-1)!}$$

Part a): get $\sigma = \ln g$ in Stirling approx'n
Straightforward (3 lines)

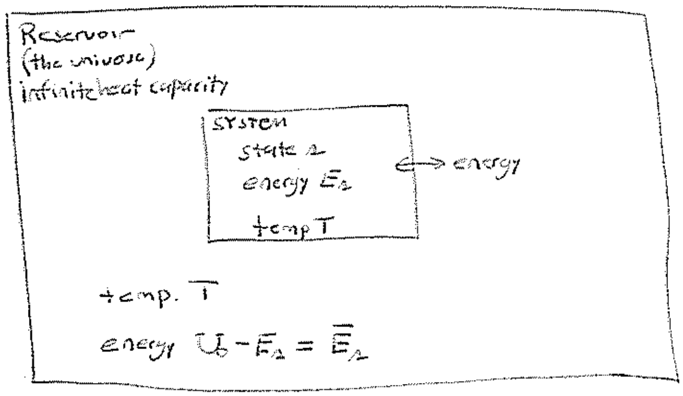
$\sigma = \frac{1}{k_B} S$

$\tau = k_B T$

part b): Using $\frac{1}{\tau} = \left(\frac{\partial \sigma}{\partial U}\right)_N$, solve for U
straightforward if you're careful
8 lines

When finished, it might be useful to sketch $U(\tau)$

CANONICAL ENSEMBLE



possible energy levels of SYSTEM are

$E_1, E_2, \ldots$ assume all distinct (just to simplify math)

to determine: prob. $\mathbb{P}(E_s, T)$ that system is in state s

$$\sum_s \mathbb{P}(E_s, T) = 1$$ because the system must be in some state

To find $\mathbb{P}(E_s)$, fix s. Then

multiplicity $g_{total} = g_{sys} \cdot g_{reservoir}$, but since we know s, $g_{sys} = 1$.

$g = g_{reservoir} \equiv g_r(\bar{E}_s)$, $\bar{E}_s = U_0 - E_s$

$\mathbb{P}(E_s) \propto g_r(\bar{E}_s) = \exp\left(\frac{1}{k_B}\bar{S}(\bar{E}_s)\right)$ where reservoir entropy $\bar{S} = k_B \ln g_r$

Consider states s_1 & s_2 w/ nearly same energies...
What is ratio of their probabilities?

$$\frac{\mathbb{P}(E_{s_2})}{\mathbb{P}(E_{s_1})} = \exp\left[\frac{1}{k_B}\left(\bar{S}(\bar{E}_{s_2}) - \bar{S}(\bar{E}_{s_1})\right)\right] \equiv \exp\left[\frac{1}{k_B}\Delta\bar{S}\right]$$

change in energy of system $\Delta E = E_{s_2} - E_{s_1}$
" " " " reservoir $\Delta\bar{E} = -\Delta E$

Since $\Delta\bar{E}$ is a small quantity, we may write

$$\Delta\bar{S} \approx \left(\frac{\partial\bar{S}}{\partial\bar{E}}\right)_N \Delta\bar{E}$$

$\bar{S}$ is a func. only of $\bar{E}$, so the partial is really a full derivative

$$= \frac{1}{T}\Delta\bar{E}$$

$$= -\frac{1}{T}\Delta E$$

Plug in:

$$\frac{\mathbb{P}(E_{s_2})}{\mathbb{P}(E_{s_1})} = \exp\left[-\Delta E/(k_B T)\right] \text{ so } \boxed{\mathbb{P}(E_s) \propto \exp\left[-E_s/(k_B T)\right] \text{ Boltzmann factor}}$$

absolute prob. : $\boxed{\mathbb{P}(E_s) = \dfrac{\exp\left[-E_s/(k_B T)\right]}{Z}}$

where $\boxed{Z = \sum' \text{Boltzmann factors} = \sum_s' \exp\left[-E_s/(k_B T)\right]}$

Partition function

"Z" for Zusammen

㉒

1/22/03

Fri: laws
canonical ensemble

today: heat & work in the canonical ensemble

Fri: heat capacity, ideal gas

μcanonical ensemble (Ch 2): fixed U, all microstates equally likely

Canonical ensemble (Ch 3, problem 4 just turned in): U can be exchanged with a reservoir at fixed T

$$P_j = \text{Prob. of micostate } j = \frac{e^{-E_j/(k_B T)}}{Z} \qquad \tau = k_B T$$

$$Z = \sum_{\substack{\text{states}\\ j}} e^{-E_j/(k_B T)}$$

average of any quantity x: $\langle x \rangle = \sum_j x_j P_j = \dfrac{\sum_j x_j e^{-E_j/(k_B T)}}{Z}$

trivial example: $\langle 2 \rangle = \dfrac{\sum_j 2 e^{-E_j/(k_B T)}}{\sum_j e^{-E_j/(k_B T)}} = 2$

less trivial: (do hw. 2.4 ?)

Another expression for U directly from Z (eqn. 3.12):

$$\tau^2 \frac{\partial}{\partial \tau} \ln Z = \tau^2 \frac{\partial Z/\partial \tau}{Z} = \tau^2 \frac{\sum_j (-\tau)^{-2}(-E_j)\, e^{-E_j/\tau}}{Z}$$

$$= \frac{\sum_j E_j\, e^{-E_j/\tau}}{Z} = \langle U \rangle$$

easier: write $Z = \sum_n e^{-\varepsilon_n \beta}$

$$U = \langle \varepsilon \rangle = \sum_n \frac{\varepsilon_n e^{-\varepsilon_n \beta}}{Z} \qquad \text{where } \beta = \frac{1}{\tau} = \frac{1}{k_B T}$$

$$= -\frac{1}{Z}\frac{\partial}{\partial \beta} Z$$

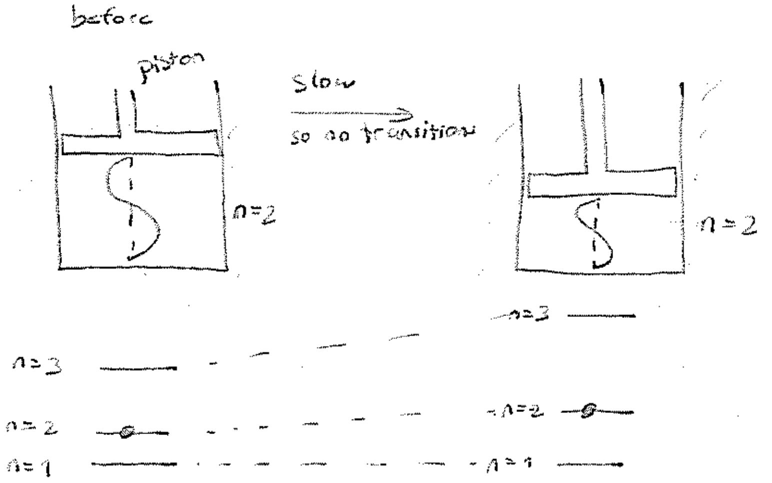
$$= -\frac{\partial}{\partial \beta}(\ln Z)$$

$$= \tau^2 \frac{\partial}{\partial \tau} \ln Z$$

Reversible processes: entropy of universe not changed

two special cases: 1) isentropic (adiabatic) : entropy of system not changed

— quantum states map on to each other



Energy has increased, but # microstates same ⇒ entropy unchanged

2) isovolumetric (isochoric)

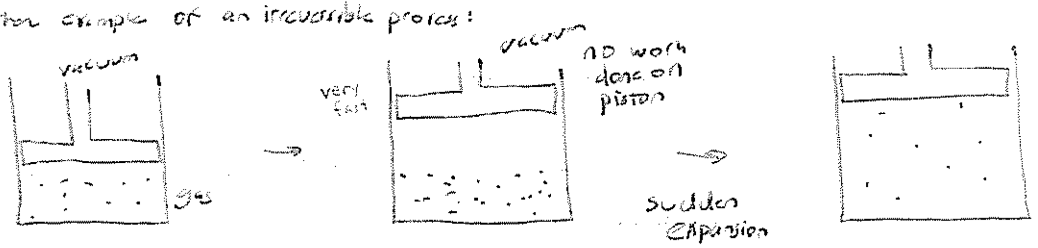
Add an infinitesimal amount of heat –

more energy ⇒ more microstates available ⇒ S of system increases

(reversible ⇐ S of reservoir decreases)

Reservoir @ at T only infinitesimally higher than that of system (else irreversible)

Another example of an irreversible process:



more about this later

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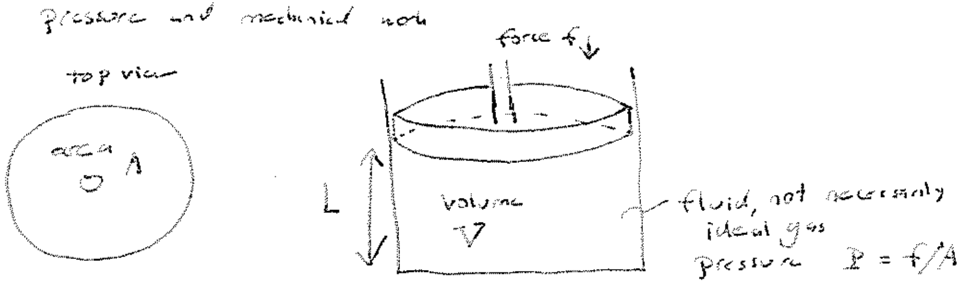
pressure and mechanical work



We'll change volume by means of a piston, which changes just one of the 3 dims. Assume U, V good state variables (N fixed), so it doesn't matter <u>how</u> we change V (so long as it's not too fast). Book changes shape in all 3 dims.

Move piston slowly – not accelerating $\Rightarrow$ |force of gas on piston| = |force of piston on gas|
$= PA$.

work done on gas $= (\Delta U)_{\mathcal{S}}$ adds energy to gas
<u>without</u> change in entropy (see above)

ΔL small, so assume F constant

$$= F\cdot(-\Delta L)_{\mathcal{S}} \qquad \text{compression: } \Delta L < 0$$
$$= -PA\cdot(\Delta L)_{\mathcal{S}}$$
$$= -P(\Delta V)_{\mathcal{S}}$$
$$\text{or} \quad P = -\left(\frac{\Delta U}{\Delta V}\right)_{\mathcal{S}} = -\left(\frac{\partial U}{\partial V}\right)_{\mathcal{S}} \qquad \mathcal{S} = k_B\,\sigma$$

State vars. U, V, N – N fixed, so just U, V
$\mathcal{S} = \mathcal{S}(U, V)$

infinitesimal change in $\mathcal{S}$ could involve <u>both</u> dU and dV, so

$$d\mathcal{S} = \left(\frac{\partial \mathcal{S}}{\partial U}\right)_{V,N} dU + \left(\frac{\partial \mathcal{S}}{\partial V}\right)_{U,N} dV \qquad \left(\text{later}, + \left(\frac{\partial \mathcal{S}}{\partial N}\right)_{U,V} dN\right)$$

I'll drop N subscripts until later chapter.

Can we choose $dU = (\delta U)_{\mathcal{S}}$ and $dV = (\delta V)_{\mathcal{S}}$ together such that there's no change in entropy of system?

$$d\mathcal{S} = 0 = \left(\frac{\partial \mathcal{S}}{\partial U}\right)_V (\delta U)_{\mathcal{S}} + \left(\frac{\partial \mathcal{S}}{\partial V}\right)_U (\delta V)_{\mathcal{S}}$$

$$\left(\frac{\partial \mathcal{S}}{\partial V}\right)_U = -\underbrace{\left(\frac{\partial \mathcal{S}}{\partial U}\right)_V}_{T^{-1}} \underbrace{\frac{(\delta U)_{\mathcal{S}}}{(\delta V)_{\mathcal{S}}}}_{\left(\frac{\partial U}{\partial V}\right)_{\mathcal{S}} = -P}$$

$$\text{so} \quad \boxed{P = T\left(\frac{\partial \mathcal{S}}{\partial V}\right)_U}$$

Going back to $d\mathcal{S}$,

$$d\mathcal{S} = \underbrace{\left(\frac{\partial \mathcal{S}}{\partial U}\right)_V}_{T^{-1}} dU + \underbrace{\left(\frac{\partial \mathcal{S}}{\partial V}\right)_U}_{P/T} dV$$

mult. by T: $\boxed{dU = TdS - PdV}$ thermodynamic identity

Interpretation: $-PdV$ is $\boxed{\text{work}}$ done on gas

TdS is $\boxed{\text{heat}}$ added to gas

Heat is work and work is heat (1st law of Thermo.)

The thermodynamic identity makes U a function of S and V: $U = U(S,V) \Rightarrow dU = \underbrace{\left(\frac{\partial U}{\partial S}\right)_V}_{T} dS + \underbrace{\left(\frac{\partial U}{\partial V}\right)_S}_{-P} dV$

1/2[illegible]

Physicists like minimization principles. E.g., in QM, we're often interested in minimizing the energy, U. Why? We imagine a system in thermal contact with a reservoir at $T=0$, or at least very cold, so that as much as possible of the energy flows into reservoir.

If we're at non-0 T, we don't minimize U — e.g., problem 2.4, where only MMM minimized energy, but was not the most probable state.

Define $\boxed{\text{Helmholtz free energy}}$ $F = U - TS = U - \tau\sigma$

intuitive meaning / motivation: lower U is good, but so is higher S.

At $T=0$, $F=U$, so only energy counts

As $T\uparrow$, maximizing S becomes increasingly important.

Does it succeed?

(*) $dF = dU - TdS - SdT$

1/21/04

$\overset{\text{by thermo. iden.}}{=} -PdV - SdT$, so $F = F(V,T)$. →

Thus, at equilibrium, if $dT = dV = 0$, we have $dF = 0$.

If we hold T const., $dF = dU - TdS$.

If we also hold V const., $dF = 0$ by 1st law

⇒ F has an extremum at equilibrium

book shows that it's a minimum.

Context: F is the "thermodynamic pot'l" when $dT = dV = 0$. There are others $= dN$ for different processes (e.g., $dT = dP = 0$ → Gibbs)

two consequences of (*) and thermodynamic identity:

Since $dF = -PdV - SdT$,

1) constant volume → $dV = 0$

$$\left(\frac{\partial F}{\partial T}\right)_V = -S$$

2) constant temperature → $dT = 0$

$$\left(\frac{\partial F}{\partial V}\right)_T = -P$$

or $P = \underbrace{-\left(\frac{\partial U}{\partial V}\right)_T}_{\text{"energy pressure"}} + \underbrace{T\left(\frac{\partial S}{\partial V}\right)_T}_{\text{"entropy pressure"}}$ for isothermal process

1/24/03 Wed: $U = \langle E \rangle = \frac{\sum E_j e^{-E_j\beta}}{Z}$

$P = -\left(\frac{\partial U}{\partial V}\right)_S = T\left(\frac{\partial S}{\partial V}\right)_U$

$dU = TdS - PdV$

today: Helmholtz F

polymers

Problems

Mon.: ideal gas
UV catastrophe

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finish old

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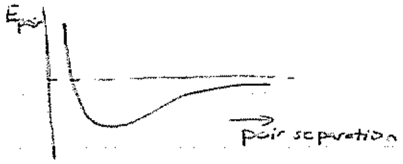
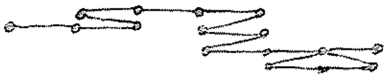
problem 3.10

Most solids expand when heated:



However, polymers — pseudo-1-dim'l — shrink.

Model: random walk – each link as likely +1 as −1 (purely entropic model – no energy)



minus "pressure" = string tension

1 dim'l TD identity $dU = TdS + \underbrace{f\,dl}_{\text{right units: dyne}\cdot\text{cm = erg}}$

"volume" = length

Instead of $P = +T\left(\frac{\partial S}{\partial V}\right)_U$, we get

$$f = -T\left(\frac{\partial S}{\partial l}\right)_U.$$

GOAL: calculate string tension f as function of temperature

a) with N links, each of length ρ, how many ways are there to get ~~total~~ length l?

No diff. from ±1 binary-spin problem

$$l = |N_+ - N_-|\rho \equiv 2|s|\rho \qquad s \text{ is "link" excess}$$

$$g(N, \pm s) = \frac{N!}{(\frac{1}{2}N+s)!\,(\frac{1}{2}N-s)!}$$

This is →
K&K point of
view – if chain
is anchored, maybe,
don't double (necessarily) –
however, addition of log 2
doesn't [illegible]
affect tension [illegible]

We don't care if it's $+s$ or $-s$, so

$$G \equiv g(N,-s) + g(N,+s) = \frac{2N!}{(\frac{1}{2}N+s)!\,(\frac{1}{2}N-s)!}$$ is relevant multiplicity.

b) In Gaussian approx., $G = 2g(N,0)\,e^{-2s^2/N}$

$$S' = k_B \ln G = k_B\left[\ln(2g(N,0)) - 2s^2/N\right] = k_B\left[\ln(2g(N,0)) - \frac{\ell^2}{2\rho^2 N}\right]$$

c) String tension $f = -T\left(\frac{\partial S}{\partial \ell}\right)_U$ No energy U at all in this model, only entropy

$$= -T k_B (-1)\frac{\ell}{\rho^2 N}$$

DEMO

$$\boxed{f = k_B T\ell/(\rho^2 N)}$$

T↑ → tension↑ → curl up

(To get equilibrium length we'd need a more realistic model with U in it.)

Getting F directly from Z w/o having to calc. S or U:

$$\boxed{U = F + TS = F - T\left(\frac{\partial F}{\partial T}\right)_V}$$

outer: a diff. eqn. for F, which book solves to get $F = -k_B T \ln Z$

Here's an alternative derivation, but it relies on an identity. Let $w_\alpha = \frac{e^{-\beta E_\alpha}}{Z}$ be the prob. of being in state α. Then

$$\boxed{S = -k_B \sum_\alpha w_\alpha \ln w_\alpha}$$

Don't think it's in K+K, but it's a very important form – starting point for information theory (computer science)

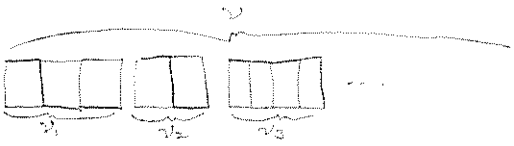
Proof: Use canonical ensemble with total of ν systems
(out of Mandl ch. 2)

$\nu_1 = \nu w_1$ of them are in state 1

$\nu_2 = \nu w_2$ of them ... state 2

$\vdots$

total ν



$\frac{\nu!}{\nu_1!(\nu-\nu_1)!}\cdot\frac{(\nu-\nu_1)!}{\nu_2!(\nu-\nu_1-\nu_2)!}\cdots$

$$g_{\text{ensemble}} = \frac{\nu!}{\nu_1!\,\nu_2!\cdots}$$

$$S_{\text{ensemble}} = k_B \ln g_{\text{ens.}} = k_B\left[\ln(\nu!) - \sum_\alpha \ln(\nu_\alpha!)\right]$$

$$\approx k_B\left[\nu\ln\nu - \nu - \sum_\alpha(\nu_\alpha \ln \nu_\alpha - \nu_\alpha)\right] \quad \text{Stirling}$$

$$= k_B\left[\nu \ln \nu - \sum_\alpha \nu_\alpha \ln \nu_\alpha\right] \quad \text{since } \sum_\alpha \nu_\alpha = \nu$$

Now write $\sum_\alpha \nu_\alpha \ln \nu_\alpha = \sum_\alpha \nu w_\alpha \ln(\nu w_\alpha)$

so $S_{ens} = \nu k_B \left[\ln \nu - \sum_\alpha w_\alpha (\ln \nu + \ln w_\alpha)\right]$

$$= \nu k_B \left[\ln \nu - \ln \nu \underbrace{\sum_\alpha w_\alpha}_{1} - \sum_\alpha w_\alpha \ln w_\alpha\right]$$

$$= -\nu k_B \sum_\alpha w_\alpha \ln w_\alpha$$

extensive

but $S' = \dfrac{S'_{ens}}{\nu}$, so $\boxed{S' = -k_B \sum_\alpha w_\alpha \ln w_\alpha}$

Now to get F.

$$S = -k_B \sum_\alpha w_\alpha \ln\left(\frac{e^{-\beta E_\alpha}}{Z}\right)$$

$$= -k_B \sum_\alpha w_\alpha \cdot \left(-\beta E_\alpha - \ln Z\right)$$

$$= \frac{+k_B}{k_B T} \underbrace{\sum_\alpha w_\alpha E_\alpha}_{U} + k_B \ln Z \underbrace{\sum_\alpha w_\alpha}_{1}$$

$$= \frac{U}{T} + k_B \ln Z$$

$$TS = U + k_B T \ln Z$$

$$U - TS = \boxed{\begin{aligned} &-k_B T \ln Z \\ = \; &F = \end{aligned}}$$

Talking points on problems:

1) Give them $Z = 1 + e^{-\beta\varepsilon}$

Show how to get U directly (NOT the way problem asks them to do):

$$U = \langle \varepsilon \rangle = \frac{0 + \varepsilon e^{-\beta\varepsilon}}{Z} = \frac{\varepsilon e^{-\beta\varepsilon}}{1 + e^{-\beta\varepsilon}} = \frac{\varepsilon}{e^{\beta\varepsilon} + 1}$$

Use this as a check.

1/23/04

2) This M is magnetization per unit volume

$\frac{N}{V} = n$ number density

Let $\varepsilon_\uparrow = -mB$ (for one spin)

$\varepsilon_\downarrow = +mB$

$Z = \left(e^{mB\beta} + e^{-mB\beta}\right)^N$ explain why

$= \left(2 \cosh[mB\beta]\right)^N$

I did this problem essentially same way as #1.

Review of hyperbolic funcs.:

$\cosh x = \frac{e^x + e^{-x}}{2}$; $\frac{d}{dx} \cosh x = \frac{e^x - e^{-x}}{2} = \sinh x$ (note: no − sign)

$\frac{d}{dx} \sinh x = \cosh x$

$\cosh^2 x - \sinh^2 x = 1$

$\frac{\sinh x}{\cosh x} = \tanh x$

$\operatorname{sech} x = \frac{1}{\cosh x}$

$\tanh^2 x = 1 - \operatorname{sech}^2 x$

$\frac{d}{dx} \tanh x = \operatorname{sech}^2 x$

3) remember ident. from last week $t^0 + t^1 + t^2 + \ldots = \frac{1}{1-t}$ for $0 < t < 1$.

1/27/03 last week:

pressure $P = -\left(\frac{\partial U}{\partial V}\right)_S = T\left(\frac{\partial S}{\partial V}\right)_U = -\left(\frac{\partial F}{\partial V}\right)_T = -\left(\frac{\partial U}{\partial V}\right)_T + T\left(\frac{\partial S}{\partial V}\right)_T$

only for reversible process $dU = T\,dS - P\,dV$ = heat + work

Helmholtz $F = U - TS = -k_B T \ln Z$

$S = -k_B \sum_\alpha w_\alpha \ln w_\alpha$ $\quad (w_\alpha = e^{-\beta E_\alpha}/Z)$

U = internal energy
T = temp.
S = entropy
Z = partition func.

today: heat capacity, ideal gas
Wed.: UV catastrophe + Planck

Heat Capacity $C_V = T\left(\frac{\partial S}{\partial T}\right)_V$ per KBK [Note: they use same symbol (!) for dimensionless heat capacity, $\tau\left(\frac{\partial \sigma}{\partial \tau}\right)_V$]

Units: $K \frac{J/K}{K} = J/K$

i.e., how much HEAT per unit change in TEMP.

Ask: which is easier to heat, air or water?

H_2O: large $\frac{C_V}{\text{volume}}$, air: small $\frac{C_V}{\text{volume}}$

In chemistry, $C_p = T\left(\frac{\partial S}{\partial T}\right)_p$ more important (expts usually @ const. pressure)

$C_V \neq C_p$

gases: noticeably different
liquids: somewhat different [ideal liq: $dV = 0$, so $C_V = C_p$]
solids: barely different, so people usually use C_V, which is easier to calc.

KBK don't properly define or motivate C_V, so I'll fill that in.

$\boxed{C_V \equiv \left(\frac{\bar{d}Q}{dT}\right)_V}$ heat flow into body per unit temp. change

heat flow $\bar{d}Q$ not a full differential, because there's no defined "Q"

For a reversible process, $\bar{d}Q = T\,dS$ — the heat term in $dU = T\,dS - P\,dV$

In general, $\bar{d}Q \leq T\,dS$

from which $\left(\frac{\bar{d}Q}{dT}\right)_X \equiv T\left(\frac{\partial S}{\partial T}\right)_X$ for any thermo. variable X (except S or T)

so $X = V$,

$\rightarrow \boxed{C_V = T\left(\frac{\partial S}{\partial T}\right)_V}$

Since $dU = T\,dS - P\,dV$, @ constant V, $(dU)_V = T(dS)_V$ (heat only)

divide by $(dT)_V$: $\left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$

thus $\boxed{C_V = \left(\frac{\partial U}{\partial T}\right)_V}$

set $X = P$: $\boxed{C_P = \left(\frac{\text{đ}Q}{dT}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P}$

Note that $C_P \neq \left(\frac{\partial U}{\partial T}\right)_P$. Instead, consider

$U = U(T, P, N)$ ← N is fixed, but we need it here, since an extensive quantity cannot be a function only of intensive quantities

(so V and S are also funcs. of N, T & P).

Aside: any two vars. out of S, T, V, P, U determine the others. ~~if at least one is extensive~~, so it doesn't work for T & P. (Remember: N is fixed)

Then $dU = \left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP$. Same for dV

$$T\,dS = \text{đ}Q = \underbrace{dU}_{} + \underbrace{P\,dV}_{}$$

$$= \overbrace{\left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP} + \overbrace{P\left[\left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP\right]}$$

Fix P, so that $dP = 0$. Then

$$\text{đ}Q\big|_P = \left[\left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P\right] dT\big|_P$$

$$\boxed{C_P = \left(\frac{\text{đ}Q}{dT}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P}$$

$$\equiv \left(\frac{\partial H}{\partial T}\right)_P \qquad \text{where enthalpy } H = U + PV$$

---

specific heat $c = \begin{cases} C/\text{mass} \\ C/\text{volume} \\ C/\text{number} \\ C/\text{number-of-moles} \end{cases}$ depending on book

example calc. of C_V: see K+K pp 62–63

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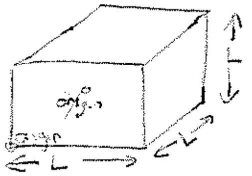
Ideal gas : non-interacting (or almost — need to be able to exchange energy with walls until equilibrium reached. Once the gas has reached equilibrium, there is no longer any net exchange of energy, so we can turn off even this weak interaction.)



Difference between interacting and non-interacting particles in a box
$N = \#$ particles spinless, ea. of mass M

interacting : $\mathcal{H} = \left[-\frac{\hbar^2}{2M}\left(\nabla_1^2+\nabla_2^2+\dots+\nabla_N^2\right) + V(\vec r_1, \vec r_2, \dots, \vec r_N)\right] \Psi(\vec r_1, \vec r_2, \dots, \vec r_N)$
$\mathcal{H}\Psi = E\Psi$

much too hard

non-interacting : $\mathcal{H}_i = -\frac{\hbar^2}{2m}\nabla_i^2 \psi_i(\vec r_i)$, $\mathcal{H} = \sum_i \mathcal{H}_i$
$\mathcal{H}\psi_i = \epsilon_i \psi_i$

Solution : $\psi_i(\vec r_i) = A\sin(n_{xi}\pi x/L)\sin(n_{yi}\pi y/L)\sin(n_{zi}\pi z/L)$,

$n_x, n_y, n_z > 0$
wave func. guaranteed to vanish at $x, y, z =$ ~~$\pm L/2$~~ $0, L$

$$\mathcal{H} = \sum \mathcal{H}_i$$
$$\Psi = \begin{Bmatrix}\text{sym.}\\ \text{antisym.}\end{Bmatrix}\left(\psi_1(\vec r_1)\,\psi_2(\vec r_2)\cdots\psi_N(\vec r_N)\right)$$

total energy $E = \sum_i \mathcal{E}_i$

$$\mathcal{E}_i = \frac{\hbar^2}{2M}\left(\frac{\pi}{L}\right)^2\left(n_{xi}^2+n_{yi}^2+n_{zi}^2\right)$$

1/27/05

Partition function for <u>1 atom</u> (set $i=1$ and drop most of subscripts i)

$$Z_1 = \sum_{n_x}\sum_{n_y}\sum_{n_z} \exp[-\beta\mathcal{E}] \overset{\text{classical}}{\approx} \iiint_0^\infty dn_x\,dn_y\,dn_z \exp[-\alpha^2(n_x^2+n_y^2+n_z^2)]$$

where $\alpha^2 \equiv \beta\frac{\hbar^2}{2M}\left(\frac{\pi}{L}\right)^2$

$$Z_1 = \left(\int_0^\infty dn\, e^{-\alpha^2 n^2}\right)^3 \underset{\substack{\text{Gaussian}\\ \text{integral:}\\ \text{appendix}}}{=} \frac{\pi^{3/2}}{8\alpha^3}$$

$$= L^3\left(\frac{\pi\, 2M}{\beta\hbar^2\pi^2 4}\right)^{3/2} = V\left(\frac{M\tau}{2\pi\hbar^2}\right)^{3/2} \equiv \frac{n_Q}{n} \qquad \text{with } n = \frac{1}{V} = \text{concentration } (\#\,\text{density})$$

Since Z_1 dimensionless, n_Q also has units of concentration:

"quantum concentration" $\qquad n_Q = \left(\frac{M\tau}{2\pi\hbar^2}\right)^{3/2}$

If $n \ll n_Q$, gas is essentially classical

If $n \gtrsim n_Q$, QM indispensable (some states may try to have multiple occupation, and QM has s.t. to say about that)

Thermal avg. energy $\quad U_1 = k_B T^2\left(\frac{\partial \ln Z_1}{\partial T}\right)_V \qquad$ (p22 of notes, 1/22/03)

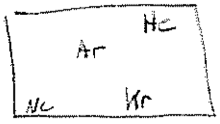
$$= \tau^2\left(\frac{\partial \ln Z_1}{\partial \tau}\right)_V$$

$$= \tau^2 \frac{1}{Z_1}\frac{3}{2}\frac{1}{\tau}Z_1 = \frac{3}{2}\tau = \boxed{\frac{3}{2}k_B T}$$

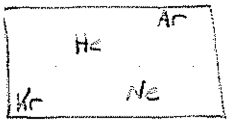
1/31/05 1/24/04

energy for a gas of 1 atom $\longrightarrow$ $\frac{\text{energy}}{\text{atom}}$ for ideal gas

If we had 1 atom of He, 1 of Ne, 1 of Ar, 1 of Kr, etc., then



and



would be different configurations, so

partition function would be $\quad Z = \sum_{\vec{n}_1}{}' \sum_{\vec{n}_2}{}' \cdots \sum_{\vec{n}_N}{}' e^{-\beta(\mathcal{E}_1+\mathcal{E}_2+\mathcal{E}_3+\cdots+\mathcal{E}_N)}$

$$= \left(\sum_{\vec{n}_1} e^{-\beta\mathcal{E}_1}\right)\left(\sum_{\vec{n}_2} e^{-\beta\mathcal{E}_2}\right)\cdots\left(\sum_{\vec{n}_N} e^{-\beta\mathcal{E}_N}\right)$$

$$= Z_1 Z_2 Z_3 \cdots Z_N .$$

However, typically we have only one kind of atom, and the two boxes above (with all the atoms He) are the same config. Since we've overcounted, divide by $N!$:

$$\boxed{Z = \frac{Z_1^N}{N!}} = \frac{1}{N!}(n_Q V)^N$$

Dividing by $N!$ resolved the "Gibbs paradox," in which the entropy comes out wrong (see problem 5). This trick is OK so long as prob. of multiple occupancy of a single state is low. Correct treatment Ch. 6, 7.

Free energy $F = -k_BT\ln Z = -Nk_BT\ln Z_1 + k_BT\underbrace{\ln(N!)}_{\approx N\ln N - N}$

$$= -Nk_BT\ln(n_Q V) + k_BT(N\ln N - N)$$

pressure $P = -\left(\frac{\partial F}{\partial V}\right)_T = Nk_BT\frac{n_Q}{n_Q V} = Nk_BT/V$

or $\boxed{PV = Nk_BT}$ ideal-gas law

note that QM drops out here and [illegible]

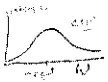
1/29/03 Mon.: C_V, C_P

$PV = Nk_BT$

today: UV catastrophe, Planck

~~[illegible]~~ Fri: thermal radiation, other massless Bosons

① A body warmer than its surroundings gives off light — most light ~~at~~ near a particular freq. characteristic of the body's temperature (e.g., red hot...)



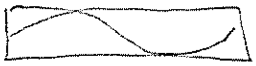
Can we understand this?

classical equipartition: energy in each mode $= \frac{1}{2}k_BT$ (e.g., $U = \frac{3}{2}Nk_BT$ in ideal gas: $3N$ modes)

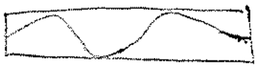
energy in Hohlraum (1 dim)

$\mathcal{E}_0 = \underset{\text{polarizn}}{2}\int\left(\frac{E^2}{8\pi} + \frac{B^2}{8\pi}\right)dV = 2\left[\frac{1}{2}k_BT + \frac{1}{2}k_BT\right] = 2k_BT$

note: cgs (Gaussian) units



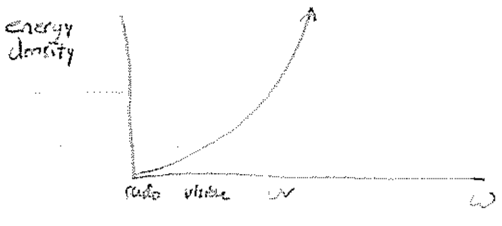
$\mathcal{E}_1 = 2k_BT$



$\mathcal{E}_2 = 2k_BT$

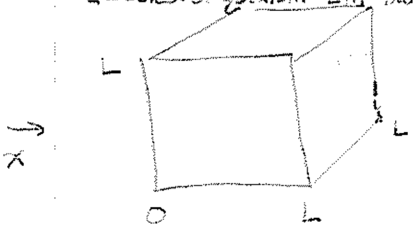
total energy $\mathcal{E} = \infty\, k_BT$ not good

Careful classical treatment by Rayleigh & Jeans



Starts ~~[illegible]~~ agreeing with expt.

classical or quantum EM modes in a cavity w/ conducting walls — cube of side L:



To solve:

sourceless Maxwell (Gaussian units)

$$\left.\begin{aligned}\nabla\cdot E &= \nabla\cdot B = 0\\ \nabla\times E &= -\frac{1}{c}\frac{\partial B}{\partial t}\\ \nabla\times B &= \frac{1}{c}\frac{\partial E}{\partial t}\end{aligned}\right\}\quad \begin{aligned}c^2\nabla^2 E &= \frac{\partial^2 E}{\partial t^2} = -\omega^2 E\\ c^2\nabla^2 B &= \frac{\partial^2 B}{\partial t^2} = -\omega^2 B\end{aligned}$$

wave eqns

standing-wave solution:

$$E_x = \overset{\text{arbitrary}}{E_{x_0}} \sin\omega t \underbrace{\cos(n_x\pi x/L)}_{\substack{\text{comes from}\\ \text{b.c. on } \vec{B}\\ \text{at surface}\\ (B_\perp = 0)}} \sin(n_y\pi y/L)\sin(n_z\pi z/L)$$

$E_x = 0$ at ∥ faces $(y, z = 0, L)$

$$E_y = E_{y_0}\ \cdots$$
$$E_z = E_{z_0}\ \cdots$$

Constraint on choice of $\vec{E}_{x_0}, E_{y_0}, E_{z_0}$:

$$0 = \nabla\cdot E \Rightarrow E_{x_0} n_x + E_{y_0} n_y + E_{z_0} n_z \equiv \vec{E}_0\cdot\vec{n} = 0$$

similarly, $\vec{B}_0\cdot\vec{n} = 0$. Furthermore, $|\vec{E}_0| = |\vec{B}_0|$ by curl parts of Maxwell.

With $\vec{E}_0$ & $\vec{n}$ fixed → 2 choices for $\vec{B}_0$.

dispersion:

$$c^2\nabla^2 E = \frac{\partial^2 E}{\partial t^2}$$

$$\frac{c^2\pi^2}{L^2}(n_x^2 + n_y^2 + n_z^2)\vec{E} = \omega^2\vec{E}$$

mode labeled by 3 ints.

$$\omega(n_x, n_y, n_z) = \frac{c\pi}{L}\sqrt{n_x^2 + n_y^2 + n_z^2}$$

equipartition → serious trouble

Planck: drop freedom to put any energy in each mode.

mode $\omega_{\vec{n}} = \omega(n_x, n_y, n_z)$:

possible energies

Classical: $\mathcal{E} = \int\left(\frac{E_0^2}{8\pi} + \frac{B_0^2}{8\pi}\right)dV \propto E_0^2$, continuous

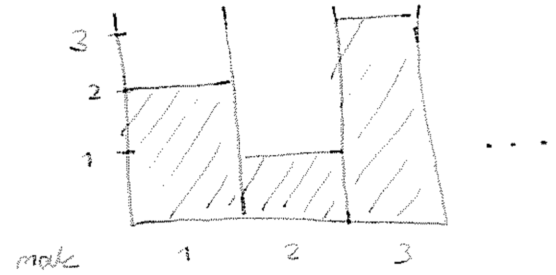
Planck: $\mathcal{E} = s\hbar\omega_n$, $s = 0, 1, 2, \ldots$

He thought in terms of interaction between $\vec{E}+\vec{B}$ & atomic states in walls (ad lib. on atomic spectra & attempts to explain them via oscillators); now we quantize the fields themselves & add $\frac{1}{2}$ to n, so $\mathcal{E}=(n+\frac{1}{2})\hbar\omega$ — back to ∞ "zero-point" energy — QED needed to make sense of it.

$\omega_{\vec{n}}$: the "n^{th}" mode of the cavity

$n_{\vec{n}}$: occupation # of the n^{th} mode
= # photons in n^{th} mode

QM way to count occupation #s:



The modes, not the photons, are the physical objects. It makes no sense to name a "particular" photon Fred and ask in which mode Fred sits.

Note: photons have no rest mass, so they're easy to create and destroy (subject to conservation of energy, momentum, and angular momentum).

THERE ARE NO PARTICLES IN QM, only fields (modes, states). Each field has an occupation number.

When we say "one photon" or "one electron," it's shorthand for a mode with some occupation number. If an e^- makes a transition from one mode (state) to another, we really mean that one mode's occup. # up by 1, another's down by 1.

Stat. mech. of photon modes

Photon modes called Bosonic after Sathyanarayana Bose — each mode may have any occupation number. Further, massless → total occupation number not conserved.

partition func. for mode $\vec{n}$

$$Z = e^{-\frac{1}{2}\hbar\omega_{\vec{n}}\beta} + e^{-\frac{3}{2}\hbar\omega_{\vec{n}}\beta} + e^{-\frac{5}{2}\hbar\omega_{\vec{n}}\beta} + \dots = \sum_{n=0}^{\infty} \exp\left(-\left[n+\tfrac{1}{2}\right]\hbar\omega_{\vec{n}}\beta\right)$$

$$= \frac{e^{-\frac{1}{2}\hbar\omega_{\vec{n}}\beta}}{1-\exp(-\hbar\omega_{\vec{n}}\beta)}$$

prob. n^{th} mode has occup^n # s $= P(s_n) = \dfrac{\exp(-s\hbar\omega_n\beta)\, e^{-\frac{1}{2}\hbar\omega\beta}}{Z}$

thermal avg: $\langle s_n\rangle = e^{-\frac{1}{2}\hbar\omega_n\beta} \sum_{s=0}^{\infty} \dfrac{s\exp(-s\hbar\omega_n\beta)}{Z} = \dfrac{e^{-\frac{1}{2}\hbar\omega_n\beta}}{Z}\left(-\dfrac{1}{\omega_n\beta}\right)\dfrac{d}{d\hbar}\sum_{s=0}^{\infty}\exp(-s\hbar\omega_n\beta)$

$$= \frac{-e^{-\frac{1}{2}\hbar\omega_n\beta}}{\omega_n\beta Z}\underbrace{\frac{d}{d\hbar}\frac{1}{1-e^{-\hbar\omega_n\beta}}}_{\frac{(-1)\omega_n\beta\, e^{-\hbar\omega_n\beta}}{(1-e^{-\hbar\omega_n\beta})^2}}$$

ω should ≈ ω_n

$$\left[\langle s_n\rangle = \frac{e^{-\frac{1}{2}\hbar\omega\beta}e^{-\hbar\omega\beta}}{(1-e^{-\hbar\omega\beta})^2}(1-e^{-\hbar\omega\beta})e^{\frac{1}{2}\hbar\omega\beta}\right.$$

$$\left.= \frac{1}{e^{\hbar\omega\beta}-1}\right]$$

$\Leftrightarrow$ classical limit: $k_BT \gg \hbar\omega$ [so that discreteness of levels $\equiv$ invisible]

$\rightarrow \langle s\rangle \simeq \dfrac{1}{1+\hbar\omega\beta-1} = \dfrac{k_BT}{\hbar\omega}$

avg. energy in mode n $\approx \hbar\omega\langle s\rangle = k_BT$

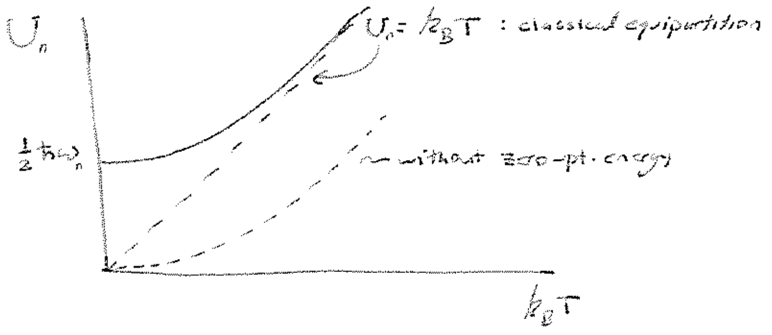
EQUIPARTITION ($\frac{1}{2}k_BT$ kinetic + $\frac{1}{2}k_BT$ potential)

$\frac{1}{2}mv^2$ $\qquad$ $\frac{1}{2}kx^2$

avg. energy in mode $\vec{n}$

$U_{\vec{n}} = \langle E\rangle = \left[\langle s\rangle + \frac{1}{2}\right]\hbar\omega_n = \left[\dfrac{1}{e^{\hbar\omega\beta}-1} + \dfrac{1}{2}\right]\hbar\omega_n$ $\quad$ ($\approx k_BT$ if $k_BT \gg \hbar\omega$)

(Go to next order in Taylor expansion: the ½ cancels out.)



subtract zero-point energy $\frac{1}{2}\hbar\omega$, p dotted)

excl. zero-pt., $\quad U_{total} = \underset{\text{polarization}}{2}\sum_{n_x,n_y,n_z} U_{\vec{n}} = 2\sum \dfrac{\hbar\omega_n}{\exp[\hbar\omega_n\beta]-1}$

Replace Σ w/ ∫

$$\sum_{\substack{n_x\geq 0\\ n_y\geq 0\\ n_z\geq 0}} \approx \frac{1}{8}\int_0^{\infty}dn\int_0^{\pi}d\theta\int_0^{2\pi}d\varphi\, n^2\sin\theta \qquad \text{where } n^2 = n_x^2+n_y^2+n_z^2$$

$$= \frac{1}{8}\int 4\pi n^2\, dn$$

㊳

SKIP if Planck first! [Plug in $\omega_{\vec{n}} = \frac{c\pi}{L} n$, $L^3 = V$ (volume)

maybe do after Planck

$$U_{total} \underset{\text{see both}}{=} V \frac{\pi^2}{15\hbar^3 c^3} (k_B T)^4$$

or energy density in cavity $\frac{U}{V} = \frac{\pi^2}{15\hbar^3 c^3} (k_B T)^4$

$\propto T^4$: Stefan-Boltzmann

Go back to integral over n to find out how much energy density @ each freq.:

maybe do FIRST

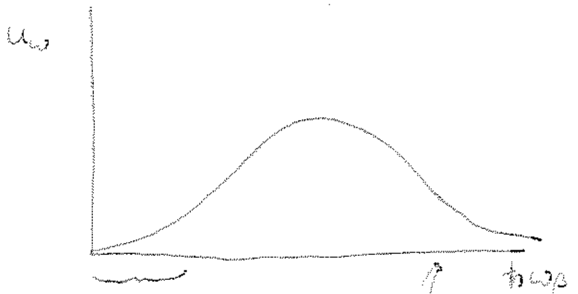
$$\frac{U}{V} = \frac{\pi}{V} \int_0^\infty dn\, n^2 \frac{\hbar\omega_n}{\exp(\hbar\omega_n\beta) - 1}$$

Change vars.: $n = \frac{L}{\pi c}\omega = \frac{V^{1/3}\omega}{\pi c}$ [[illegible] $\omega_n = \frac{c\pi}{L} n$]

$$\frac{U}{V} = \frac{\pi}{V} \hbar \int_0^\infty \frac{V\omega^3}{\pi^3 c^3} \frac{1}{\exp(\hbar\omega\beta) - 1} d\omega$$

$$\equiv \int_0^\infty d\omega\, u_\omega$$ where $u(\omega) = \frac{\text{energy}}{\text{volume} \cdot \text{frequency}}$ = spectral density

$$= \boxed{\frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{\exp(\hbar\omega\beta) - 1}}$$ Planck radiation law



starts out like Rayleigh-Jeans

but no ultraviolet catastrophe (we've subtracted zero-pt.)

(39)

1/31/03 Wed: UV catastrophe

today: Planck

[illegible]: Debye - phonons - C_V

PROBABLY SKIP PAGE OR JUST SUMMARIZE

How hot is orange hot?

Say peak of Planck @ 600nm

$$0 = \frac{du_\omega}{d\omega} = \frac{1}{\hbar\beta}\frac{du_\omega}{dx} \quad , \quad x = \hbar\omega\beta$$

$$= (\text{const.})\frac{d}{dx}\frac{x^3}{e^x - 1} = (\text{const.})\left(\frac{3x^2}{e^x-1} - \frac{x^3 e^x}{(e^x-1)^2}\right)$$

so $3(1 - e^{-x}) = x$

zero at $x_0 = 2.82$ (numerical)

$$\omega = \frac{2\pi c}{600nm} = \frac{\pi\, 6\cdot 10^{10}\,\frac{cm}{sec}}{6\cdot10^2\cdot10^{-7}cm} = \pi\cdot10^{15}sec^{-1}$$

$\hbar = 1.1\cdot10^{-27}$ erg sec

so $\beta = \frac{x_0}{\hbar\omega} = \frac{2.82}{\hbar\omega} = 8.2\cdot10^{11}\,erg^{-1}$

$k_B = 1.4\cdot10^{-16}$ erg/K

$\Rightarrow T \approx 8800K$

$k_B T = \frac{1}{\beta} = \frac{\hbar\omega}{2.82} \sim \hbar\omega \cdot$ const. of order 1

? too hot per se way?

It's correct, although we might perceive this as "bluehot"

~~Reason: distrib'n rather than single number, write $u(x)$ = const. $\frac{x^3}{e^x-1}$ [illegible]~~

$$\int_0^\infty u_\omega\, d\omega = \int_0^\infty u_\lambda\, d\lambda$$

$\omega = \frac{c}{2\pi\lambda}$, so $d\omega = -\frac{c}{2\pi}\lambda^{-2}d\lambda$

thus $u_\omega \neq u_\lambda$, and they don't even have their maxima at same place

(i.e.; $\omega_{max} \neq \frac{c}{2\pi\lambda_{max}}$)

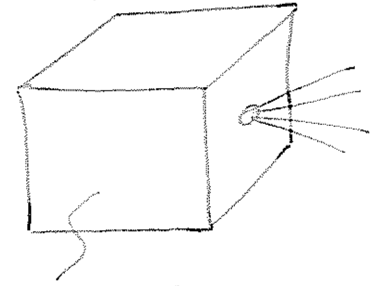
do integrals → λ_{max} = given by

$$x' = \frac{hc}{T\lambda_{max}} = 4.965$$

so if ~~[illegible]~~ most important wavelength is 600nm, $T \approx 3500K$

(40)

Blackbody radiation



perfectly reflecting walls do not emit (perfect: incoming light reflects elastically: neither gains nor loses energy)

flux density $J_U = \frac{\text{total power}}{\text{area of hole}}$: $\frac{\text{erg/sec}}{\text{cm}^2}$ or $\frac{\text{Watt}}{m^2}$

or $\frac{\text{BTU}}{\text{fortnight furlong}^2}$

$J_U \propto \frac{U}{V}$ energy density in Hohlraum

$J_U \propto c$ faster to get energy out

proportionality factor turns out to be $\frac{1}{4}$ (prob. 4.45)

so $J_U = \sigma_B T^4$

$\sigma_B = \frac{\pi^2 k_B^4}{60\hbar^3 c^2}$ } Stefan-Boltzmann law

$\approx 5.670 \cdot 10^{-5} \frac{\text{erg/sec}}{\text{cm}^2 K^4}$

Black body: perfect absorber of light (that doesn't mean no emission: at equilibrium, blackbody emits as much as it absorbs. So to test whether something is a blackbody, we need non-equilibrium light - e.g., flashlight).
Small hole is ideal black surface because very little of the incident radiation will be reflected back.

Consider non-black puck

absorbtivity $0 \leq a \leq 1$: 0 means perfect reflector, like walls
1 means black, like hole

Anything not absorbed is reflected, so $a = 1 - r$, r = reflectivity

How much does puck emit? Put it in front of hole, wait for equilibrium. It's continually absorbing energy from the Hohlraum at a rate a times that of ~~a~~ a black body. For there to be equilibrium, it must give up the same flux. Thus emissivity = a, i.e, flux density from a non-black body is

1/31/03

$a J_U$ (0 for perfect reflector).

This is why thermal insulation for $\overset{\text{unmanned}}{\text{space}}$ probes consists of nothing but layers of highly reflective metal foil. Foil also used in low-T physics, where ΔT very large so $T_h^4 - T_l^4$ most significant source of heat flow. Also in windows of office bldgs, etc.

1/31/04

(41)

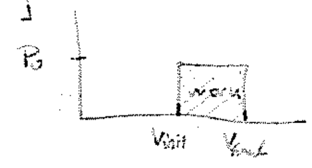
2/3/03

Fri.: Planck

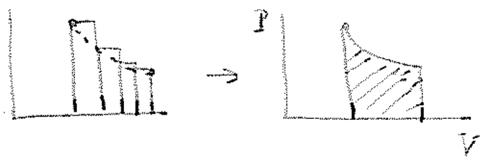
today: applications – Nyquist – phonons

Wed.: Gibbs distribution, chem. pot.

∃ some questions about problem 1 — work done by gas on piston @ constant pressure $= P_0(V_{final} - V_{init})$



If P & V both change,



isotherm: $PV = Nk_BT = n^{chem.}RT = \text{const.}$

finish old notes (##) – first recall Stefan-Boltzmann $J_J = a\sigma_B T^4$ (a=absorbtivity)

porty - 3.5K ≅ 1K

right: see Wilson's ✓ Nobel lecture

opt. ~~more atmosphere transp?~~

Q. The cosmic black-body radiation was discovered in 1965 – 2.7 K, almost isotropic. Knowing nothing at all about the experimental apparatus, you should nonetheless be able to guess one liquid that was essential for more accurate measurements later

A. liq. helium @ 4.2 K, evaporative cooling → ~1K. If expt. isn't cooler than 2.7K, how can it see 2.7K (except maybe by calorimetry).

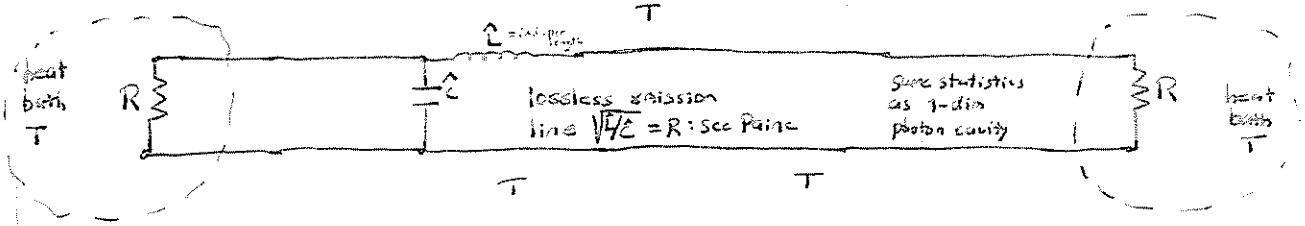
Q. Why can we see TV, radio, which is even colder?

A. non-equilibrium energy density. TV snow! radio static ⇐ blackbody

---

Nyquist / Johnson noise in a resistor with zero mean current ($\langle I\rangle = 0$)

V should be zero $\langle V\rangle = 0$, but there will be fluctuations: $\langle V^2\rangle \neq 0$.

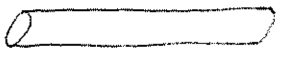


obviously not right – Nyquist made more careful

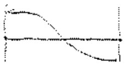
across each resistors $V = \frac{2IR}{~~2R~~}$ since we have two resistors

explain 2R (Nyquist's 1928 argument): EMF (V) from either resistor sees resistance 2R and so drives current $I = \frac{V}{2R}$

Think of line as a 1-dim. cavity



L will drop out: use it just for counting.



Allowed modes have wavelengths $\lambda_n = \frac{2L}{n}$, $n = 1, 2, 3, \ldots$

so (non-angular) frequencies $f_n = \frac{c'}{\lambda_n} = \frac{c'n}{2L} \equiv n\,\delta f$, $\delta f = \frac{c'}{2L}$

$c' = \frac{1}{\sqrt{\mathcal{L}\mathcal{C}}}$ prop. speed

two modes for each freq., one right-moving, one left

so in freq. range Δf, # allowed modes $= \frac{\Delta f}{\delta f} = \frac{2L}{c'}\Delta f$

Ave. energy in mode of freq. $\omega_n = 2\pi f_n$ is

$$\frac{\hbar\omega_n}{e^{\hbar\omega_n\beta}-1} = \frac{hf_n}{e^{hf_n\beta}-1} \qquad \text{where} \quad h = 2\pi\hbar$$

If $k_BT \gg hf_n$, classical equipartition $\rightarrow k_BT$ per mode (Taylor)

Justification:

e.g., say it's a computer circuit — don't measure freq. > GHz $\sim 10^{12}s^{-1}$

$\hbar\omega \sim 10^{-27}$ erg sec $\cdot\, 10^{12}$ sec $\sim 10^{-15}$ erg

$k_B = 1.4 \cdot 10^{-16}$ erg/K,

so equiv. temp ~ 10K

would have been much lower for a radio-freq. or lower circuit ($\sim$MHz)

So in freq. range Δf, energy is $\frac{\Delta f}{\delta f} \cdot k_BT = 2\Delta f \frac{L}{c'} k_BT$

Total energy over all freqs. blows up for same reason as Rayleigh-Jeans – at high freq., we need to use QM instead of equipartition. Note this means computer designers also getting close to having to use QM.

Rate at which energy goes to left resistor

$$\simeq \underbrace{\frac{1}{2}}_{\frac{1}{2}\text{ modes going left}} \cdot \underbrace{\frac{\text{energy in line}}{L}}_{\text{linear energy density}} \cdot \underbrace{c'}_{\text{speed (group velo.)}} = \Delta f\, k_BT$$

same rate to right

$Z = R$, so no power reflected.

power generated inside left resistor and sent to line $\overset{\text{per freq.}}{=} P_0$

power absorbed from line by left resistor $= P_0 \quad = \Delta f \, k_B T$

power absorbed in a resistor $= \langle I^2 \rangle R$

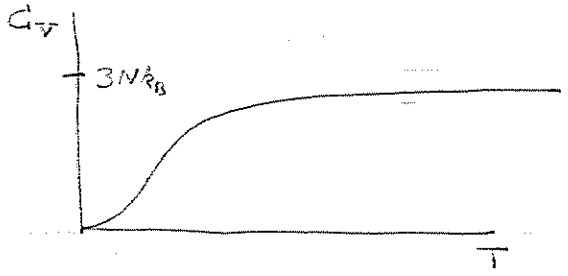
$$= \frac{1}{4R} \langle V^2 \rangle \quad \text{since } I = \frac{V}{R+R} \text{ in this problem}$$

thus $\boxed{\langle V^2 \rangle = 4R\Delta f \, k_B T}$ Nyquist / Johnson noise

Example of "fluctuation-dissipation theorem"
$\langle V^2 \rangle$ is fluctuation
power in R is dissipation.

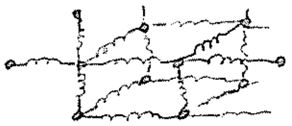
2/9/05

Heat capacity in insulating solids



high-temp. $3Nk_B$, "Law of du Long & Petit," is just classical equipartition.

[better drawing in rough draft]



N = # atoms, not # molecules

$$\left.\begin{array}{l} 3N \text{ positional deg. of freedom} \\ 3N \text{ momentum} \end{array}\right\} 6N \times \tfrac{1}{2} k_B T \rightarrow \boxed{U = 3Nk_B T}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = 3Nk_B \quad (\text{as noted before, } C_V \approx C_P \text{ for solids})$$

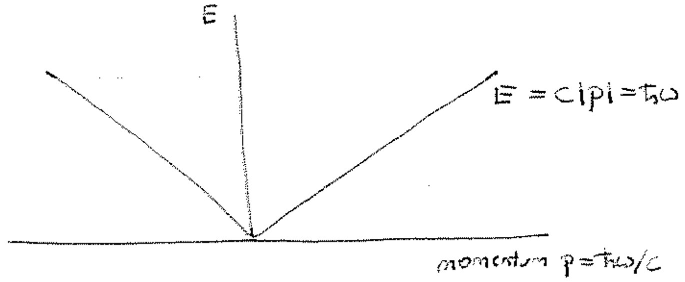
Volumetric specific heat $c_v = \frac{C_V}{V} = 3nk_B$, $\quad n = \frac{N}{V}$ = number density

well established experimentally but fails at low T. How low depends on material – typically 100-300K

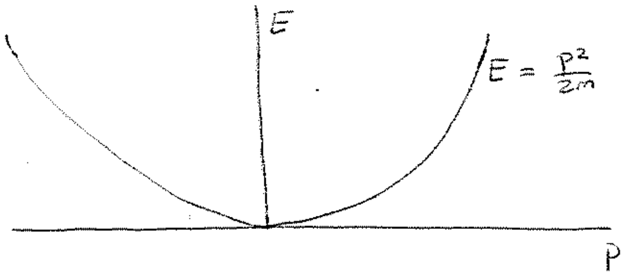
Dispersion curves
group velocity $v = \frac{1}{\hbar}\frac{\partial E}{\partial k} = \frac{\partial E}{\partial p}$

Comparison of light & elastic modes of solids:

light

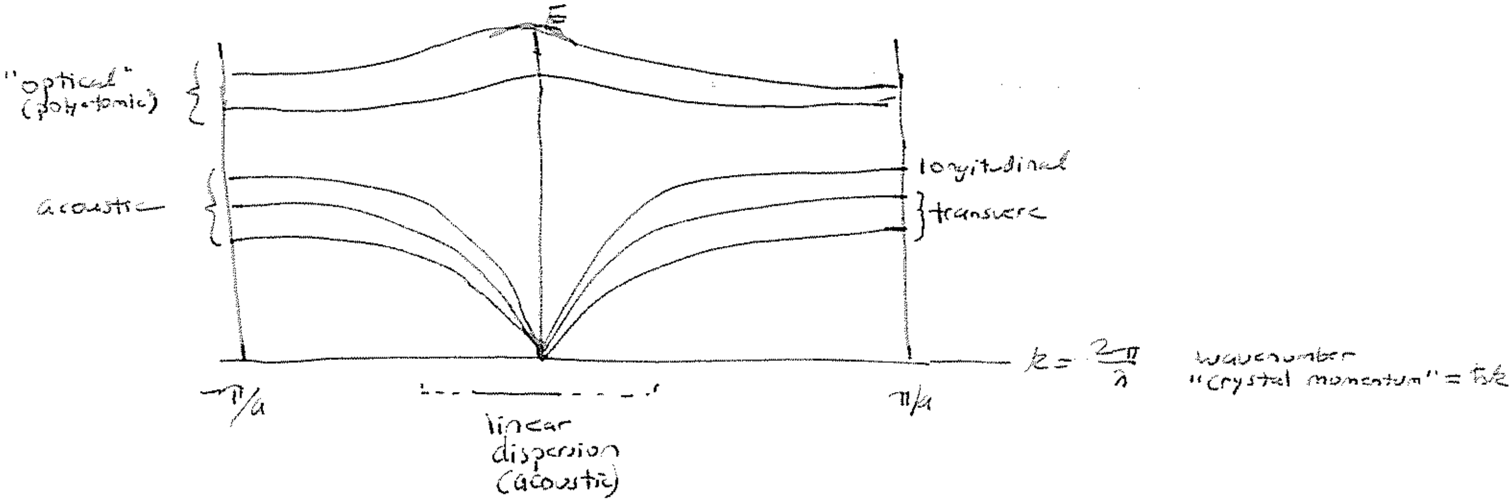


"relativistic dispersion"

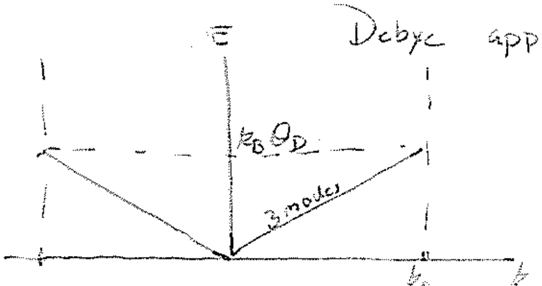


for massive free particle
(non-relativistic)

result from solid-state physics:



maximum wavenumber because of minimum distance between atoms
$|\lambda| \geq 2a$
$\Rightarrow |k| \leq \pi/a$



Debye approx.:
1) ignore "optical" modes
2) assume all 3 acoustic branches have equal velo, v
3) carry integration exactly as far as needed to get 3N modes

2/5/03 Mon.: Nyquist, phonons
today: heat cap. of insulating solid,
Chem. pot.
Fri: Chem. pot., Gibbs

Group velocity $v = \frac{1}{\hbar}\frac{\partial E}{\partial k} = \frac{\partial E}{\partial p}$

Recall photon integral: (P37)

$$\overset{\text{polarization}}{2}\sum_{n_x,n_y,n_z} = \frac{2}{8}\int_0^\infty 4\pi n^2\,dn$$

$n \propto \omega \propto k$ since we have linear dispersion so that v ind. of k
Integral over n is really over k

For Debye $\boxed{\text{phonons}}$ v again ind. of k, so we can again replace $\int dk$ with $\int dn$.
Multiply photon result by 3/2 since there are three polarizations instead of just two,
and cut off integral:

Fix cutoff by $\frac{3}{8}\int_0^{n_D} 4\pi n^2\,dn = 3N$, $n = \frac{L\omega}{\pi v} = \frac{kL}{\pi}$ L box side – will drop out

$$\frac{1}{2}\pi n_D^3 = 3N$$

$$n_D = (6N/\pi)^{1/3}$$

$$U = \sum \langle \varepsilon_n \rangle = \sum \frac{\hbar\omega}{\exp(\hbar\omega\beta)-1} \quad , \quad \omega = \frac{n\pi v}{L}$$

$$= \frac{3}{2}\pi\int_0^{\omega_D}\left(\frac{\pi v}{L}\right)^3\omega^2\,d\omega\,\frac{\hbar\omega}{\exp(\hbar\omega\beta)-1} \qquad \omega_D = \frac{n_D\pi v}{L}$$

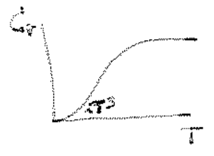
For low-temp. limit, $k_B T \ll k\theta_D \equiv \hbar\omega_D$, integrand is tiny when $\omega \gtrsim \omega_D$,
so might as well take integral all the way to ∞. Now it's essentially
the same as for photon gas (but 3/2)

$$U \approx \frac{3}{2}\pi\left(\frac{\pi v}{L}\right)^3\left(\frac{1}{\hbar\beta}\right)^3\frac{1}{\beta}\left(\frac{\pi^4}{15}\right)$$

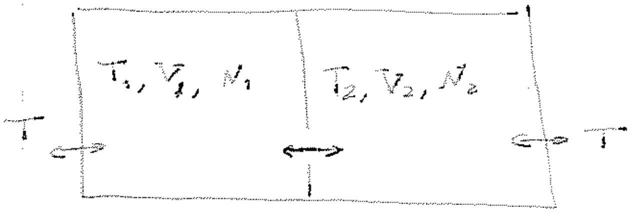
$$\overset{\text{algebra}}{=} \frac{3\pi^4 N k_B T^4}{5\,\theta_D^3}$$

low-temp. heat cap. $C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{12}{5}\pi^4 N k_B\,(T/\theta_D)^3$

high-temp limit recovers Dulong & Petit $3Nk_B T$



Until now, we've held N (# particles) constant, and two thermodynamic variables determined all the others (e.g. U and V, or V and T). Clearly, adding a particle while holding V, T constant <u>will</u> change U, P, S, etc., so we need to consider this.



We already know that $T_1 = T_2 = T$ (in equilibrium)

Write Helmholtz free energy: $F_i = F(T, V_i, N_i) = U(T, V_i, N_i) - TS(T, V_i, N_i)$ for each system $(i = 1, 2)$

note: U, S, F all determined by ind. vars. T, V_i, N_i

Since T_i, V_i fixed,

$$dF_1 = \left(\frac{\partial F_1}{\partial N_1}\right)_{T,V} dN_1$$

and

$$dF_2 = \left(\frac{\partial F_2}{\partial N_2}\right)_{T,V} dN_2 = -\left(\frac{\partial F_2}{\partial N_2}\right)_{T,V} dN_1$$

Total change in free energy $dF = \left[\left(\frac{\partial F_1}{\partial N_1}\right)_{T,V} - \left(\frac{\partial F_2}{\partial N_2}\right)_{T,V}\right] dN_1$

At equilibrium, $dU = dS = 0$, so $dF = 0$. A particle is as likely to move $1 \to 2$ as $2 \to 1$, so $[\cdot] = 0$. Write

① $\boxed{\text{Chemical potential}}$ $\mu(T, V, N) \equiv \left(\frac{\partial F}{\partial N}\right)_{T,V}$ for each; deduce $\mu_1 = \mu_2$ in equilibrium.

Since particles are not infinitely divisible, maybe in place of ① we should write

$$\mu(T, V, N) = F(T, V, N) - F(T, V, N-1) \approx \left(\frac{\Delta F}{\Delta N = 1}\right)_{T,V}$$

so chem. pot. is free energy difference due to adding one particle.
In general, μ depends on N, so

$$\mu \neq F/N$$

Chapter 8 defines Gibbs free energy $G = U - TS + PV = F + PV$, and we'll see that

② $$\mu(T, P) = \left(\frac{\partial G}{\partial N}\right)_{T,P} = G(N, T, P)/N$$

since at constant T & P, μ is ind. of N.

When to use ① and when ②?

① useful for boxes of fixed volume;

② useful in chem. reactions open to atmosphere held at fixed pressure

example: ideal gas

$$F(T, V, N) \overset{\text{ch. 3}}{=} -k_B T \left[N \ln Z_1 - \ln N!\right]$$

Z_1 = part. func. one particle

$= n_Q V$

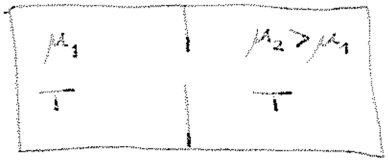
$$F(T, V, N-1) = -k_B T\left[(N-1)\ln Z_1 \underbrace{- \ln((N-1)!)}_{-\ln N! + \ln N}\right]$$

subtract $$\mu(T, V, N) = k_B T \ln\left(\frac{N}{n_Q V}\right) = k_B T \ln(n/n_Q)$$, $n = \frac{N}{V}$ number density

$$n_Q = \left(\frac{m k_B T}{2\pi\hbar^2}\right)^{3/2}$$

- intensive (like n, T, P)
- at fixed volume, increases, but nonlinearly, with N

If $\mu_2 > \mu_1$, particles will flow — in which direction?



Since $n_2 > n_1$, more likely $\boxed{2 \to 1}$ than reverse

Call this source of chem. pot. "internal" (μ^{int})
We can counteract it w/ an "external" potential.

For example, for particles all with charge e, apply an electric potential φ to side 1, zero to side 2. This raises energy of ea. particle in system 1 by $e\varphi$ but doesn't change entropy.

Now $F_1 = F_1^{old} + N_1 e\varphi$

$$\mu_1^{tot} = \left(\frac{\partial F_1}{\partial N_1}\right)_{T,V} = \left(\frac{\partial F_1^{old}}{\partial N_1}\right)_{T,V} + e\varphi = \mu_1^{int} + e\varphi$$

If we set $e\varphi = \mu_2^{int} - \mu_1^{int}$, then $\mu_1^{tot} = \mu_2^{tot}$, and we've restored equilibrium.

K&K give several examples:

1. pressure as func. of height h in atmosphere

$$P(h) = P(0)\, e^{-h/h_c} \qquad h_c \approx 8.5\ \text{km}$$

pretend isothermal & equilibrium (!)
& ideal gas
& all N_2

$$\mu^{int} = k_B T \ln(n(h)/n_Q) \qquad \text{(ideal gas)}$$

$$\mu^{ext} = Mgh \qquad (M \approx M_{N_2})$$

$\mu(h) = \mu^{int} + \mu^{ext}$ should be ind. of height

$$0 = \frac{d\mu}{dh} = \frac{k_B T/n_Q\, dn}{n/n_Q\ dh} + Mg = \frac{k_B T}{n}\frac{dn}{dh} + Mg$$

$$\frac{dn}{dh} = \frac{-Mg}{k_B T}\, n$$

solution: $n = e^{-h/h_c}\, n(0)$ w/ $h_c = \dfrac{k_B T}{Mg}$

Since $P = \dfrac{N k_B T}{V} = n k_B T$, $P \propto n$, and

$$\boxed{P(h) = P(0)\, e^{-h/h_c}}$$

Other examples in text:

- mobile particles in B field
- Pb-acid battery

2/7/03 Wed.: chemical pot.
atmospheric pressure

today: generalize two old results to case $dN \neq 0$

$$dU = TdS - PdV \quad (1^{st} \text{ law})$$

and prob. $p(s) = \frac{e^{-\beta E_s}}{Z}$

1st excursion into Differential Land

2nd back to Ensembleville

next week: Fermi & Bose

Corrections: ① handout ② $G(N,T,P) = N\mu(T,P)$

Extend thermodynamic identity.

Consider U a function of S, V, and N

Justify: particles in a box — S defined so that lumps together all the states w/ same U

①
$$dU = \underbrace{\left(\frac{\partial U}{\partial S}\right)_{V,N}}_{T} dS + \underbrace{\left(\frac{\partial U}{\partial V}\right)_{S,N}}_{-P} dV + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN$$

What is $\left(\frac{\partial U}{\partial N}\right)_{S,V}$?

Try $F = F(T,V,N) = U - TS$

$$dF = \underbrace{\left(\frac{\partial F}{\partial T}\right)_{V,N}}_{-S} dT + \underbrace{\left(\frac{\partial F}{\partial V}\right)_{T,N}}_{-P} dV + \underbrace{\left(\frac{\partial F}{\partial N}\right)_{T,V}}_{\mu} dN$$

②
$$= -SdT - PdV + \mu dN$$

but $dF \overset{\text{also}}{=} dU - TdS - SdT$

③
$$= \overbrace{\cancel{TdS} - PdV + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN}^{} - \cancel{TdS} - SdT$$

Equate ② and ③:

$$-SdT - PdV + \mu dN = -PdV + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN - SdT$$

so $\boxed{\left(\frac{\partial U}{\partial N}\right)_{S,T} = \mu}$ answers KBK problem 5.11

and we arrive at extended thermodynamic identity $\boxed{dU = TdS - PdV + \mu dN}$ $+ \mu_2 dN_2 + \mu_3 dN_3 + \ldots$ if we have several species

Yet another expression for μ:
Consider S as a func. of U, V, N. Then

$$dS = \underbrace{\left(\frac{\partial S}{\partial U}\right)_{V,N}}_{1/T} dU + \underbrace{\left(\frac{\partial S}{\partial V}\right)_{U,N}}_{\downarrow \text{ below}} dV + \underbrace{\left(\frac{\partial S}{\partial N}\right)_{U,V}}_{\downarrow \text{ below}} dN$$

[This is [illegible]]

What is $\left(\frac{\partial S}{\partial V}\right)_{U,N}$?

I ~~have~~ know an easier way to answer this, but then I'd have no excuse to prove a useful general formula, so....

[Immediate from TD identity]

For this section, keep N fixed implicitly. S, V, U then interdependent:

$$S = S(U, V)$$
$$V = V(S, U)$$
$$U = U(S, V)$$

general identity for x, y, z interrelated: $\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$

derive: $z = z(x, y)$, so $dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$

Hold z constant (i.e., $dz = 0$): then

$$\left(\frac{\partial z}{\partial x}\right)_y dx\Big|_z = -\left(\frac{\partial z}{\partial y}\right)_x dy\Big|_z \quad \text{, or}$$

$$\boxed{\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -1}$$

Alternative derivation not using "bare" differentials ~~begins with facts~~
~~this: $\frac{dz}{dy} = \frac{dy}{dz} = \frac{dx}{dz} = 0$ since any two are independent~~

write $\frac{dy}{dy} = 1$

apply chain rule twice

$$1 = \frac{dy}{dy} = \left(\frac{\partial y}{\partial x}\right)_z \frac{dx}{dy} + \left(\frac{\partial y}{\partial z}\right)_x \frac{dz}{dy}$$
$$= 1 + \left[\left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial z}\right)_y + \left(\frac{\partial y}{\partial z}\right)_x\right] \frac{dz}{dy} \quad \text{etc.}$$

$x \to U$
$y \to V$
$z \to S$

$$\underbrace{\left(\frac{\partial U}{\partial V}\right)_S}_{-P} \left(\frac{\partial V}{\partial S}\right)_U \underbrace{\left(\frac{\partial S}{\partial U}\right)_V}_{1/T} = -1$$

(all at constant N, too)

(51)

so $\left(\frac{\partial S}{\partial V}\right)_U = P/T$

Now for $\left(\frac{\partial S}{\partial N}\right)_{U,V}$. I'll do this one the easy way:

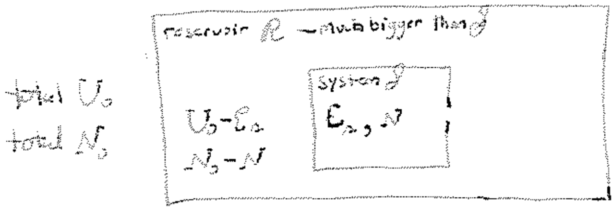
$$dS = \frac{1}{T}dU + \frac{P}{T}dV + \left(\frac{\partial S}{\partial N}\right)_{U,V} dN$$

$\times T$ ↙

$$dU = T\,dS - P\,dV - T\left(\frac{\partial S}{\partial N}\right)_{U,V} dN$$

so $\boxed{-T\left(\frac{\partial S}{\partial N}\right)_{U,V} = \mu}$

Grand-Canonical (Gibbs) ensemble



V fixed for this derivation.

ensemble: many systems $\mathcal{S}_1 = (\overset{\text{state}}{s_1}, \overset{\#\text{ particles}}{N_1})$,
$\mathcal{S}_2 = (s_2, N_2), \ldots$

[illegible]

What is prob. $p(s,N)$ that the system is in state (s,N)?

Follow same deriv'n used for canonical ensemble: $g_{\mathcal{R}+\mathcal{S}} = g_{\mathcal{R}} \cdot 1$

$$p \propto g_{\mathcal{R}}(U_0-\mathcal{E}_s,\ N_0-N) = \exp\left(\frac{1}{k_B} S(U_0-\mathcal{E}_s,\ N_0-N)\right)$$

S is entropy of $\mathcal{R}$

two states, (s_1, N_1) and (s_2, N_2):

$$\frac{p(s_1,N_1)}{p(s_2,N_2)} = \exp\left(\frac{1}{k_B}\underbrace{\left[S(U_0-\mathcal{E}_1, N_0-N_1) - S(U_0-\mathcal{E}_2, N_0-N_2)\right]}_{\Delta S}\right)$$

$$\mathcal{S} \ll \mathcal{R}, \text{ so } \frac{|N_1-N_2|}{N_0} \ll 1, \quad \frac{|\mathcal{E}_1-\mathcal{E}_2|}{U_0} \ll 1,$$

$$\text{so } \Delta S = -(\mathcal{E}_1-\mathcal{E}_2)\underbrace{\left(\frac{\partial S}{\partial U_0}\right)_{N_0}}_{1/T} - (N_1-N_2)\underbrace{\left(\frac{\partial S}{\partial N_0}\right)_{U_0}}_{-\mu/T}$$

and $$\frac{P(s_1 N_1)}{P(s_2, N_2)} = \exp\left[N_1\mu\beta - N_2\mu\beta - \mathcal{E}_1\beta + \mathcal{E}_2\beta\right]$$

$$= \frac{\exp\left[(N_1\mu - \mathcal{E}_1)\beta\right]}{\exp\left[(N_2\mu - \mathcal{E}_2)\beta\right]}.$$

and

$$P(s, N) = \frac{\exp\left[(N\mu - \mathcal{E})\beta\right]}{\mathcal{Z}}$$

$$\text{where} \quad \mathcal{Z} = \sum_{s,N}{}' \exp\left[(N\mu - \mathcal{E}_{s,N})\beta\right]$$

"Grand partition function" or "Gibbs Sum"

Note $\mathcal{E}_{s,N}$ depends on N of state s; in non-interacting system, $\mathcal{E}_{s,N} = N\varepsilon_{s,1}$

Some authors use other letters, e.g. script $\mathcal{Q}$ or Ξ

Useful expression for thermal ave. particle #

$$\langle N \rangle = \frac{\sum_{s,N} N e^{-(\mathcal{E}_s - \mu N)\beta}}{\mathcal{Z}}$$

$$\text{Recall trick} \quad U = \langle \mathcal{E}_s \rangle = \frac{\sum_s \mathcal{E}_s e^{-\mathcal{E}_s\beta}}{\sum_s e^{-\mathcal{E}_s\beta}} = -\frac{\partial}{\partial\beta}(\ln Z)$$

$$\text{or} \quad = -k_B T^2 \frac{\partial}{\partial T}(\ln Z) \quad \text{eq 3}$$

We can do something similar for $\langle N \rangle$.

$$\langle N \rangle = \boxed{k_B T \frac{\partial}{\partial\mu} \ln \mathcal{Z}}$$

μ is "conjugate" to N

Useful for fixing $n = \langle N \rangle$ to be "right" number

example: non-interacting e^-'s in a metal

If s labels states (incl. spin), each s can have occupancy # 0 or 1 only (Fermionic).

prob. of occup. of a one-e⁻ state (incl. spin), s, w/ energy $\mathcal{E}_s$ is

$$P_s = \frac{e^{-(\mathcal{E}_s-\mu)\beta}}{\mathcal{Z}_s}$$

where $\mathcal{Z}_s = 1 + e^{-(\mathcal{E}_s-\mu)\beta}$, so $P_s = \frac{e^{-(\mathcal{E}_s-\mu)\beta}}{1+e^{-(\mathcal{E}_s-\mu)\beta}} = \frac{1}{e^{(\mathcal{E}_s-\mu)\beta}+1}$

$$\mathcal{N} = \langle N \rangle = \int \underbrace{ds}_{\substack{\text{will include geometrical} \\ \text{factor - "density of states" } d\mathcal{E}}} \frac{1}{e^{(\mathcal{E}_s-\mu)\beta}+1}$$

[Go through zero-temp. occup'n.]

One then sets μ such that $\mathcal{N}$ will be right # (determined by valency).

Result from §§: $\mu = \mu(T=0) - (\text{const.})\left(\frac{k_B T}{\mathcal{E}_F}\right)^2 + \mathcal{O}(k_B T/\mathcal{E}_F)^4$

$\mathcal{E}_F$ = Fermi energy
typically $\sim k_B \cdot 10000$ K

2/6/04

2/10/03 Fri.: Gibbs
today: examples of Gibbs
Fermi-Dirac
Bose-Einstein
Boltzmann
Wed.: Ideal classical gas

non-interacting Gibbs sum $\mathcal{Z} = \sum_{s,N}' e^{-(\mathcal{E}_s-\mu N)\beta} \equiv \sum_{s,N} \lambda^N e^{-\mathcal{E}_s\beta}$

$\lambda = e^{\mu\beta}$ called "fugacity" (K&K call it "absolute activity", but I haven't seen this term elsewhere)
L. fugere - to flee   fugacious - transitory, fleeting, volatile

Recall that for an ideal gas
$\mu = k_B T \ln(n/n_Q)$, $n = \frac{N}{V}$, n_Q = quantum concentration

so $\lambda = n/n_Q$ (ideal gas)

example: K & K prob. 5.4 $\boxed{\text{read}}$ (sup'r cytoplasm!)

Set $\Delta\mu = Vq$, q the fundamental charge

Taking $\mu = k_B T \ln(n/n_Q)$ as for ideal gas (this is just an estimate), we have

$$\Delta\mu = \mu_{in} - \mu_{out} = k_B T \ln\left(\frac{n_{in}}{n_{out}}\right) = k_B T \ln(10^4)$$

useful # to remember: $k_B\, 300K \approx \frac{1}{40}\, eV$

$$\text{so } \Delta\mu \approx \frac{1}{10}\ln(10)\, eV \approx 0.23\, eV = Vq$$

$$\text{or } \boxed{V = 0.23 \text{ volts}}$$

example: K & K problem 5.8 $\boxed{\text{read}}$

3 levels:

State	energy
vacant	0
O_2	ε_A
CO	ε_B $(<\varepsilon_A)$

equilib.: μ_{O_2} of adsorbed O_2 = μ of gas-phase O_2
μ_{CO} of adsorbed CO = μ of " CO

fugacity $\lambda_{O_2} = 1\cdot 10^{-5} = e^{\mu_{O_2}\beta}$
fugacity $\lambda_{CO} = 1\cdot 10^{-7}$

$T = 37°C = 310K$ Ignore internal degrees of freedom

a) Gibbs sum for one site (no CO) is

$$\mathcal{Z} = e^0 + \lambda_{O_2} e^{-\beta\varepsilon_A} = 1 + \lambda_{O_2} e^{-\beta\varepsilon_A}$$

$$\text{prob. occupied} = \frac{\lambda e^{-\beta\varepsilon_A}}{\mathcal{Z}} \equiv 0.9 \equiv \alpha \qquad (\lambda = \lambda_{O_2})$$

$$e^{-\beta\varepsilon_A}(\lambda - \alpha\lambda) = \alpha$$

$$e^{-\beta\varepsilon_A} = \frac{\alpha}{\lambda(1-\alpha)} = \frac{0.9}{10^{-5}\cdot 0.1} = 9\cdot 10^5$$

$$\mathcal{E}_1 = -k_B T \ln(9 \cdot 10^5) = -\overbrace{8.63 \cdot 10^{-5} \frac{eV}{K}}^{k_B} \, 310K \ln(9 \cdot 10^5) = \boxed{-0.37 eV}$$

b) Introduce CO @ $\approx$ 1% the concentration of O_2 $(\lambda_{CO} = 10^{-7})$ (not exactly 1%, because λ depends on masses)

We're told that now only 10% of sites have absorbed O_2. What is CO binding energy, $\mathcal{E}_B$?

$$\mathcal{Z} = 1 + \lambda_{O_2} e^{-\beta\mathcal{E}_A} + \lambda_{CO} e^{-\beta\mathcal{E}_B} = 1 + \overbrace{9}^{\text{since } e^{-\beta\mathcal{E}_A} = 9 \cdot 10^5, \lambda_1 = 10^{-5}} + \lambda_{CO} e^{-\beta\mathcal{E}_B}$$

$$\text{prob. occ. by } O_2 = \frac{\lambda_{O_2} e^{-\beta\mathcal{E}_A}}{\mathcal{Z}} = \frac{9}{\mathcal{Z}} \equiv 0.1$$

$$\mathcal{Z} = 90, \text{ or } \lambda_{CO} e^{-\beta\mathcal{E}_B} = 80$$

$$\mathcal{E}_B = -k_B T \ln\left(\frac{80}{\lambda_{CO}}\right) = -0.0268 eV \ln(8 \cdot 10^8)$$

$$= \boxed{-0.55 eV}$$

CO much more tightly bound than O_2:

$$\frac{-(\mathcal{E}_B - \mathcal{E}_A)}{k_B T} = \frac{0.18 eV}{0.027 eV} \simeq 6.7$$

so it's very hard @ body temp. to dislodge a CO

"Quantum Statistics"

Q. Mech: every particle has an intrinsic ang. mom. that is either an integer multiple (0 OR 1) of $\hbar$ or a half-integer multiple (e.g., photon has spin 1, electron spin-1/2).

caveat: isotropy.

Spin-Statistics thm. (relativistic q. field theory):

caveat: 3 dim. in 3D space will [illegible] anyons in 2dim.

integer spin: Boson, $\Psi(2,1) = \Psi(1,2)$ (#s are labels)

half-integer: Fermion $\Psi(2,1) = -\Psi(1,2)$

consequence for Fermions:

However,

because labels are illusory

11-15

So double (or higher) occupancies are FORBIDDEN.

BOSE case. Like photons/phonons, but particle number (in general) conserved → real μ.

$\lambda = e^{\mu\beta}$

For one state ("orbital"), $\mathcal{Z} = \sum_{N=0}^{\infty} e^{-(\underset{\uparrow}{N\varepsilon} - \mu N)\beta} = \sum_{N=0}^{\infty} (\lambda e^{-\varepsilon\beta})^N = \dfrac{1}{1-\lambda e^{-\varepsilon\beta}}$

assumes non-interacting (ideal gas)

$\boxed{\text{provided } \varepsilon > \mu \text{ so } \lambda e^{-\varepsilon\beta} < 1}$

occupation function:
occup. # for ~~[illegible]~~ a single state of energy ε:

$$f(\varepsilon) = \langle N(\varepsilon) \rangle = \lambda \frac{\partial}{\partial \lambda} \ln \mathcal{Z} \qquad \left(\overset{\text{Check}}{=} \sum' \frac{\lambda^N N e^{-\varepsilon N\beta}}{\mathcal{Z}} \right)$$

$$= -\lambda \frac{\partial}{\partial \lambda} \ln(1 - \lambda e^{-\varepsilon\beta})$$

$$= \frac{\lambda e^{-\varepsilon\beta}}{1 - \lambda e^{-\varepsilon\beta}} = \frac{1}{\lambda^{-1} e^{\varepsilon\beta} - 1}$$

$$= \boxed{\frac{1}{e^{(\varepsilon-\mu)\beta} - 1}}$$

Bose-Einstein distribution

Interpretation: for a level w/ energy ε, ~~[illegible]~~ what is the expected occupation number?

FERMI case

Gibbs sum for one state ("orbital") $\mathcal{Z} = 1 + \lambda e^{-\beta\varepsilon}$

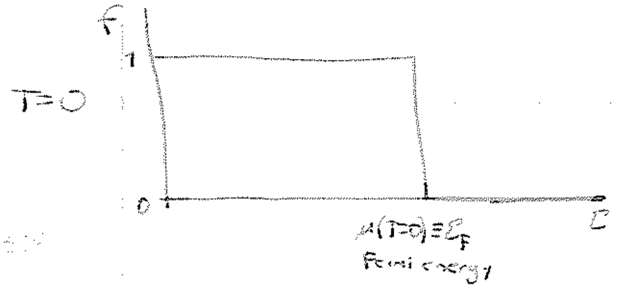
Occupation func.

$$f(\varepsilon) = \langle N(\varepsilon) \rangle = \frac{\lambda e^{-\beta\varepsilon}}{1 + \lambda e^{-\beta\varepsilon}} = \boxed{\frac{1}{e^{(\varepsilon-\mu)\beta} + 1}}$$

Fermi-Dirac distribution

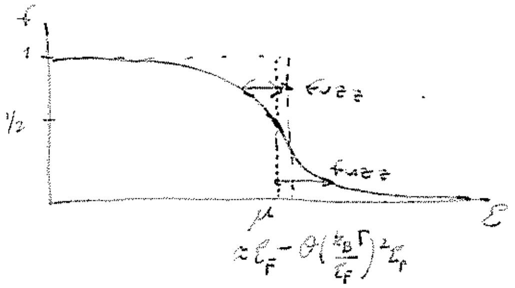
Interp.: we have many levels, ea. of a diff. energy ε. $f(\varepsilon)$ tells the prob each is occupied.

$$\text{At } T=0, \quad \beta = \infty, \text{ so } f(\varepsilon) = \begin{cases} \dfrac{1}{0+1} = 1 & \varepsilon < \mu(T=0) \quad \text{definitely occupied} \\ \dfrac{1}{\infty+1} = 0 & \varepsilon > \mu(T=0) \quad \text{definitely unoccupied} \end{cases}$$



$$\int_0^{\mathcal{E}_F} \underbrace{f(\mathcal{E})}_{1}\, \overset{\text{density of states – geometrical factor}}{g(\mathcal{E})}\, d\mathcal{E} = N$$

For $T>0$, μ is a function of T as noted on Friday



$$\int_0^{\infty} f(\mathcal{E})\, g(\mathcal{E})\, d\mathcal{E} = N$$

How big is the fuzz? Say $\mathcal{E}>\mu$.

$$f(\mathcal{E}) = \frac{1}{\sum_{j=0}^{\infty}\left(\frac{1}{j!}\left[(\mathcal{E}-\mu)\beta\right]^j\right)+1}$$

[don't [illegible] do Taylor expansion just more informative]

For the denom. not to blow up (so $f>0$), we need

$$\underbrace{(\mathcal{E}-\mu)}_{\text{fuzz}}\beta \lesssim 1 \quad , \text{so} \quad \boxed{\text{fuzz} \sim k_B T} \quad \text{(approx.)}$$

Calc. $\mathcal{E}_F$ for a typical metal – done in Ch. 7 → ~10000 K – 100000 K, so fuzz ≪ $\mathcal{E}_F$ at room temp.

2/10/03
2/9/04

replaced next page

Classical – ~~much~~ harder! book doesn't derive

limit that double occup'n is small of either f_{FD} or f_{BE}

$$\text{is} \quad \frac{1}{e^{(\mathcal{E}-\mu)\beta} \pm 0} = \boxed{\lambda e^{-\mathcal{E}\beta} \equiv f_{MB}(\mathcal{E})}$$

Let $x = (\mathcal{E}-\mu)\beta$ (dimensionless). Plot

$$f_{\substack{FD\\BE\\MB}}(x) = \frac{1}{e^{x}+a}, \quad a = \begin{cases} +1 & FD \\ -1 & BE \\ 0 & MB \end{cases}$$

point out classical regime

2/12/03

~~[illegible]~~ Mon.: $f_{FD}(\mathcal{E}) = \frac{1}{e^{(\mathcal{E}-\mu)\beta}+1}$

$f_{BE}(\mathcal{E}) = \frac{1}{e^{(\mathcal{E}-\mu)\beta}-1}$

today: $f_{MD}(\mathcal{E})$;

internal degrees of freedom

occupation funcs. for a single state at energy $\mathcal{E}$

Fri: entropy of mixing problems

Classical - not done in the book

perhaps because it's not "natural" in the classical picture to think of the occupation of a state

For state $\mathcal{E}$,

$$\mathcal{Z} = \sum_{N_\mathcal{E}} \underset{\substack{\uparrow \\ \text{prevent Gibbs} \\ \text{paradox (not} \\ \text{really legitimate)}}}{\frac{1}{N!}} \underset{\substack{\uparrow \\ \text{ideal gas}}}{e^{-(\mathcal{E}-\mu)N_\mathcal{E}\beta}} = \sum_{N_\mathcal{E}} \frac{1}{N_\mathcal{E}!}(\underset{\substack{\uparrow \\ \text{fugacity}}}{\lambda} e^{-\beta\mathcal{E}})^{N_\mathcal{E}} \overset{\text{Taylor}}{=} \exp(\lambda e^{-\beta\mathcal{E}})$$

$$\underset{\substack{\uparrow \\ \text{emphasize} \\ \text{just one state}}}{\langle N_\mathcal{E} \rangle} = -\frac{1}{\beta \mathcal{Z}}\left(\frac{\partial \mathcal{Z}}{\partial \mathcal{E}}\right)_{\mu, T}$$

[illegible] [Simplify: $\mathcal{Z} = \exp(\lambda e^{-\beta\mathcal{E}})$]

$$\text{so } \langle N_\mathcal{E} \rangle = -\frac{1}{\beta \exp(\lambda e^{-\beta\mathcal{E}})} \lambda e^{-\beta\mathcal{E}}(-\beta)\exp(\lambda e^{-\beta\mathcal{E}})$$

$$= \lambda e^{-\beta\mathcal{E}} = \boxed{e^{-(\mathcal{E}-\mu)\beta}} \equiv f_{MB}(T, \mu)$$

Let $x = e^{(\mathcal{E}-\mu)\beta}$. Then

$$f_{FD}(x) = \frac{1}{x+1}$$

$$\leftarrow \quad f_{BE}(x) = \frac{1}{x-1}$$

$$f_{MB}(x) = \frac{1}{x+0}$$

new μ measure let $x = (\mathcal{E}-\mu)\beta$ to agree w/ graph. Then $f_{FD}(x) = \frac{1}{e^x+1}$ etc

Somewhat misleading: μ is different in the three cases for the same n.

$f_{FD} \approx f_{BE} \approx f_{MB}$ when $x \gg 1 \rightarrow$ occupancy small

Now show graph. Comment on the $\frac{1}{N!}$: classical is valid only when $f_{MB} \ll 1$; i.e., only $N = 0, 1$ contribute significantly, so $\frac{1}{N!} \approx 1$ anyway.

[illegible] 11/3/12

Deduce behavior of IDEAL monatomic classical gas from f_{MB}

- we previously derived most of these relations from the canonical ens.

1. Using μ as knob to ensure $\langle N \rangle$ = true # N_0 :

$$N_0 = \langle N \rangle = \sum_{\substack{s \\ \text{states}}} f_{MB}(\mathcal{E}_s) = \lambda \sum_s e^{-\beta \mathcal{E}_s} = \lambda Z_1, \quad \text{where } Z_1 = n_Q V \quad \text{(ch. 3)}$$

So $\lambda = \frac{N_0}{Z_1} = \frac{N_0}{n_Q V} = \frac{n}{n_Q}$ (ideal gas)

taking log: $\boxed{\mu = k_B T \ln(n/n_Q)}$ previously derived in ch. 5.

2. Helmholtz free energy

$$\left(\frac{\partial F}{\partial N}\right)_{T,V} = \mu$$

$$F(N,T,V) = \int_0^N dN' \mu(N',T,V) = k_B T \left[N \ln \frac{1}{n_Q V} + \int_0^N dN' \ln N'\right]$$

from entry: $\mu = k_B T\left[\ln \frac{1}{n_Q V} + \ln N'\right]$

$$= k_B T \left[N \ln \frac{1}{n_Q V} + N \ln N - N - \underbrace{\lim_{x \to 0} (x \ln x)}_{0 \text{ by L'Hôpital}}\right]$$

$$= N k_B T \left[\ln(n/n_Q) - 1\right] \quad \text{agrees w/ ch. 3}$$

3. pressure (exactly as in ch 3): $P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \overset{n = N/V}{=} \frac{k_B T V^{-2} N^2}{(n/n_Q)\, n_Q} = \frac{N k_B T}{V}$

or $\boxed{PV = N k_B T}$

4. entropy $S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = -N k_B \left[\ln\left(\frac{n}{n_Q}\right) - 1\right] + \frac{N k_B T n_Q}{n} \left(\frac{d n_Q}{dT}\right) n_Q^{-2} n$

$$n_Q = \left(\frac{M k_B T}{2\pi\hbar^2}\right)^{3/2}, \quad \text{so} \quad \frac{d n_Q}{dT} = \frac{3}{2} n_Q / T$$

$$S = -N k_B \left[\ln\left(\frac{n}{n_Q}\right) - 1\right] + N k_B T n_Q \frac{3}{2} \frac{n_Q}{T} n_Q^{-2}$$

$$= -N k_B \left[\ln\left(\frac{n}{n_Q}\right) - 1 - \frac{3}{2}\right] = \boxed{N k_B \left[\ln\left(\frac{n_Q}{n}\right) + 5/2\right]} \quad \text{Sackur-Tetrode}$$

5. $U = F + TS = N k_B T\left[\ln(n/n_Q) - 1 + \ln(n_Q/n) + 5/2\right] = \boxed{\frac{3}{2} N k_B T}$

equipartition (discuss)

$$6.\ C_V = T\left(\frac{\partial S}{\partial T}\right)_{V,N} = \frac{Nk_BT}{n_Q/n}\,\frac{1}{n}\,\frac{dn_Q}{dT} = \boxed{\frac{3}{2}Nk_B}$$ equipartition

(or just $\left(\frac{\partial U}{\partial T}\right)_{S,N}$)

$$7.\ C_P = \left(\frac{\partial U}{\partial T}\right)_{P,N} + P\left(\frac{\partial V}{\partial T}\right)_{P,N}$$ (notes, p31, 1/27/03)

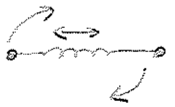
$$= \frac{3}{2}Nk_B + P\left(\frac{\partial}{\partial T}\right)_{P,N}\left(\frac{Nk_BT}{P}\right) = \frac{3}{2}Nk_B + Nk_B = \boxed{\frac{5}{2}Nk_B}$$

ratio $\frac{C_P}{C_V} \equiv \gamma = \frac{5}{3}$ for ideal monatomic gas

generally, >1.

How do we revise these results if there are internal degrees of freedom?

e.g.,



3/3/03

From before, for one "orbital" of energy ε,

$$\mathcal{Z} = \sum_N \frac{1}{N!}\left(\lambda e^{-\beta\varepsilon}\right)^N$$ (no internal deg. of freedom)

Now we need to sum over internal states as well: $\varepsilon \to \varepsilon + \varepsilon_i^{int}$

$$\mathcal{Z} = \sum_N \sum_i \frac{1}{N!}\left(\lambda e^{-\beta[\varepsilon+\varepsilon_i^{int}]}\right)^N = \sum_N \frac{1}{N!}\left(\lambda e^{-\beta\varepsilon} Z_{int}\right)^N$$

where $Z_{int} = \sum_i e^{-\beta\varepsilon_i^{int}}$

$$= \exp\left(\lambda e^{-\beta\varepsilon} Z_{int}\right)$$

occupation number for state "ε" including all internal states:

$$f_{MB}(\varepsilon) = \langle N_\varepsilon \rangle = -\frac{1}{\beta\mathcal{Z}}\left(\frac{\partial\mathcal{Z}}{\partial\varepsilon}\right)_{\mu,T} = Z_{int}\,e^{-(\varepsilon-\mu)\beta} = Z_{int}\,\lambda e^{-\varepsilon\beta}$$

Sum over all states $N = \sum_{\varepsilon} f_{MB}(\varepsilon) = Z_{int} \lambda \underbrace{\sum_{\varepsilon}' e^{-\varepsilon\beta}}_{n_Q V = \text{just } Z_1}$

so $\lambda = \dfrac{n}{n_Q Z_{int}} = e^{\mu\beta}$

$$\mu = k_B T \left[\ln(n/n_Q) - \ln Z_{int} \right]$$

$$F = \int_0^N dN' \mu(N', T, V) = \overset{\text{result w/o internal freedom}}{F_0} + F_{int} = F_0 - N k_B T \ln Z_{int}$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = S_0 - \left(\frac{\partial F_{int}}{\partial T}\right)_{V,N}$$ (need model of F_{int} to evaluate further)

2/12/03

$$U_{int} = N \frac{\sum_i \varepsilon_i^{int} e^{-\beta\varepsilon_i^{int}}}{Z_{int}} = N \langle U_{int}^{(1)} \rangle .$$

2/14/03 Wed.: $f_{\{FD, BE, MB\}}$

- Classical ideal gas ↵
- thermodynamic quantities
- internal degrees of freedom $Z_{int} = \sum_i' e^{-\beta\varepsilon_i^{int}}$

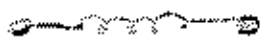
~~today~~: finish internal deg.

reversible vs. irreversible

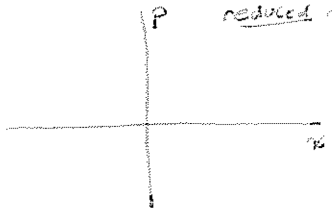
examples

Mon.: metals

neutron stars

Model just the U_{int} from  diatomic spring (not pitch or ~~roll~~ yaw)

classical 2D phase space:



p reduced momentum ; m will be reduced mass

x displacement

$$\varepsilon^{int} = \frac{1}{2} K x^2 + \frac{1}{2} \frac{p^2}{m}$$

In canonical ensemble all phase space is accessible with Boltzmann probability.

$$Z_{int} = \alpha \int_{-\infty}^{\infty} e^{-\frac{1}{2} K x^2 \beta} dx \int_{-\infty}^{\infty} e^{-\frac{1}{2}(p^2/m)\beta} dp$$

α: prop. constant of units $\dfrac{1}{\text{cm}} \cdot \dfrac{1}{\text{g cm/s}} = \dfrac{1}{\text{erg s}}$ hmm...

$$Z_{int} = \alpha \sqrt{\frac{2\pi}{\beta K}} \sqrt{\frac{2\pi m}{\beta}} = \alpha \frac{2\pi}{\beta} \sqrt{\frac{m}{K}}$$

$$\langle U_{int}^{(n)} \rangle = -\frac{1}{Z_{int}} \frac{\partial}{\partial \beta} Z_{int} = \beta \cdot \beta^{-2} = k_B T \text{ for spring}$$ α drops out
(2 degrees of freedom)

$\frac{1}{2} k_B T$ for each of pitch and ~~roll~~ yaw (nothing for ~~yaw~~ roll), so

$$U_{\text{diatomic}}^{\text{classical}} = N k_B T \Big(\underbrace{\tfrac{3}{2}}_{3 \times \text{translational}} + \underbrace{\tfrac{2}{2}}_{\text{spring}} + \underbrace{\tfrac{1}{2}}_{\text{pitch}} + \underbrace{\tfrac{1}{2}}_{\text{yaw}} \Big) = \tfrac{7}{2} N k_B T$$

So $C_V = \frac{7}{2} N k_B$

<u>NOT IN AGREEMENT</u> with expt. except at high T –
e.g. figure 3.4 p78

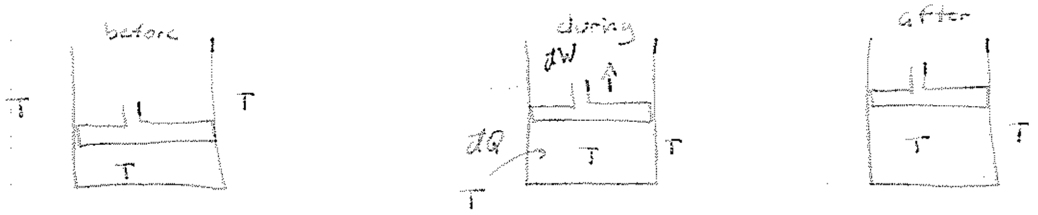
vibrations "frozen out" (q. mech.) – just means $\alpha \int dx \int dp$ should instead have been a <u>sum</u> over <u>discrete</u> states (quantum harmonic osc.)

4/5/07

Contrast several different expansion processes for monatomic ideal gas. In each case, V_i = initial volume, V_f = final vol., N = fixed.
$= \underline{2V_i}$

1. Reversible – isothermal

space above piston is vacuum;
initially held down (e.g., w/weight)
let it go up
then stop it



pressure $P_i = \frac{N k_B T}{V_i}$

$P_f = \frac{N k_B T}{V_f}$, so $\frac{P_f}{P_i} = \frac{V_i}{V_f} = \frac{1}{2}$ for this example

To find entropy change, use Sackur-Tetrode

$$S_i = N k_B \left[\ln\left(\frac{n_Q}{n_i}\right) + \frac{5}{2} \right] \qquad S_f = N k_B \left[\ln\left(\frac{n_Q}{n_f}\right) + \frac{5}{2} \right]$$

concentration $n = \frac{N}{V}$, so $n_f = \frac{1}{2} n_i$.

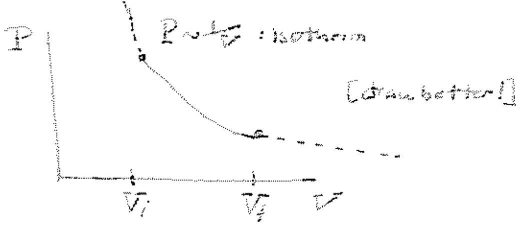
Change $\Delta S = S_f - S_i = N k_B \ln\left(\frac{n_i}{n_f}\right) = N k_B \ln 2 > 0$

$$\text{Work done by gas on piston} = \int_{V_i}^{V_f} P(V)\,dV = \int_{V_i}^{V_f} \frac{Nk_BT}{V}\,dV = Nk_BT\ln\left(\frac{V_f}{V_i}\right) = Nk_BT\ln 2$$

Change in internal energy $\Delta U = 0$ because $U_f = U_i = \frac{3}{2}Nk_BT$

Since gas lost internal energy through mechanical work, an equivalent amount of heat must have flowed in from the reservoir: $\Delta Q = Nk_BT\ln 2$.

review P-V diagram (useful for reversible processes only)

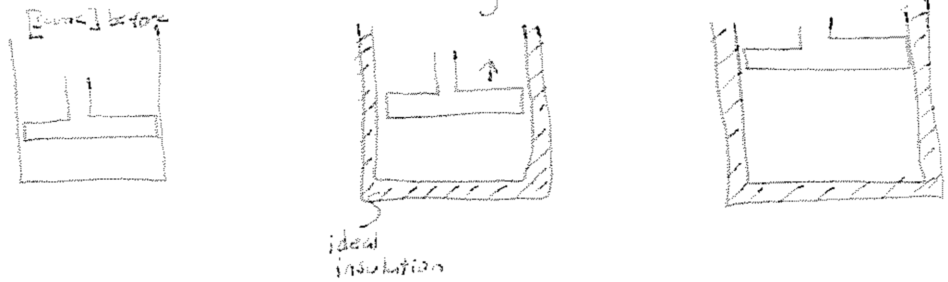


Q.: How can the process be reversible if entropy increases?
A.: Entropy change in reservoir is $-\Delta S$, so total entropy change is zero.
$\Delta Q = T\Delta S$.

2 hour

---

2. Reversible – adiabatic



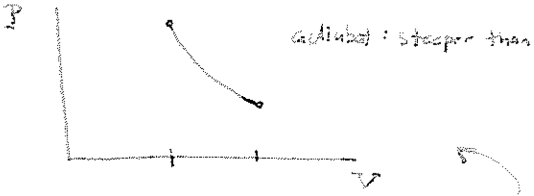
entropy change $\Delta S = 0$ by definition

Sackur-Tetrode $S(V,T) = Nk_B\left[\ln\left(\frac{n_Q V}{N}\right) + \frac{5}{2}\right] = Nk_B\left[\ln(T^{3/2}V) + \text{const.}\right]$

$n_Q = \left(\frac{m k_B T}{2\pi\hbar^2}\right)^{3/2}$

So if $S = \text{const.}$, $\boxed{T^{3/2}V = \text{const.}}$

Q. In HW, you had instead $T^3V = \text{const.}$ for an adiabatic process. What was different? A.: photon gas is ideal but not <u>classical</u>.



⑦ $$\frac{P_iV_i}{T_i} = \frac{P_fV_f}{T_f}$$

substitute $T = \alpha V^{-2/3}$ to get PV rel'n: $P_iV_i^{5/3} = P_fV_f^{5/3}$, i.e., $P \propto V^{-5/3}$

(64)

Change in temp.: from ①, $\frac{T_f}{T_i} = \frac{P_f V_f}{P_i V_i} = \frac{V_f^{-5/3} V_f}{V_i^{-5/3} V_i} = \left(\frac{V_f}{V_i}\right)^{-2/3} = 2^{-2/3} < 1$

so it cools

Change in internal energy

$$\Delta U = U_f - U_i = \frac{3}{2} N k_B (T_f - T_i) < 0$$ loses energy

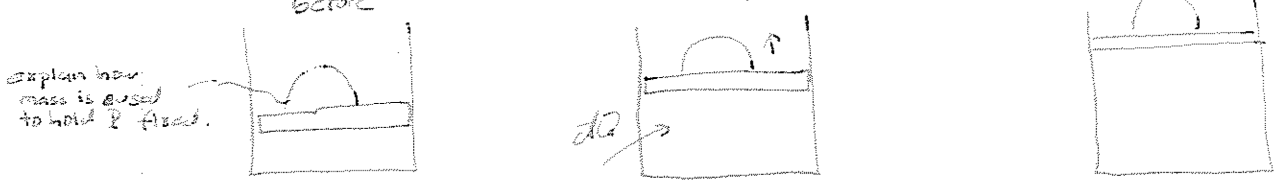
work done by gas on piston $= \int_{V_i}^{V_f} P\,dV = \int_{V_i}^{V_f} \frac{N k_B T(V)}{V}\,dV$

$\boxed{T(V) = \alpha V^{-\frac{2}{3}}}$ $= N k_B \alpha \int_{V_i}^{V_f} V^{-5/3}\,dV = -\frac{3}{2} N k_B \alpha \left(V_f^{-2/3} - V_i^{-2/3}\right) = -\frac{3}{2} N k_B (T_f - T_i) > 0$

exactly equal to change in internal energy

---

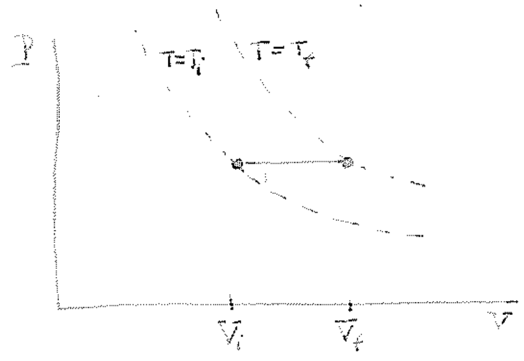
3. reversible – isobaric



explain how mass is used to hold P fixed.

reservoir T increases slowly

perhaps by means of the compression of another ideal gas



work done by gas on piston $= P(V_f - V_i)$

2/13/04

$$P = \text{const.} = \frac{N k_B T_i}{V_i} = \frac{N k_B T_f}{V_f}$$

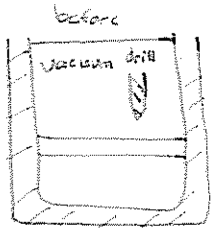
so $\frac{T_f}{T_i} = \frac{V_f}{V_i} = 2$ for this example

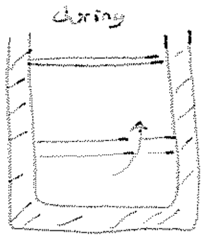
Change in internal energy $\Delta U = U_f - U_i = \frac{3}{2} N k_B (T_f - T_i) > 0$

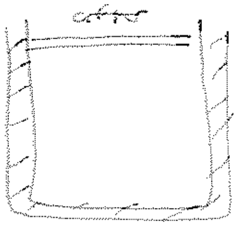
2/14/03

(65)

Contrast sudden expansion:







(or could pull up piston really fast – no work either way)

$\Delta U = 0$ because there's no nowhere for work to go

Since $U_f = U_i = \frac{3}{2} N k_B T$: no change in temperature (reminder: for ideal gas)

Increase in entropy from Sackur-Tetrode:

$$\Delta S = N k_B \ln\left(\frac{n_i}{n_f}\right) = N k_B \ln 2 \quad \text{if} \quad \frac{V_f}{V_i} = 2$$

Q. Why can't we use $dU \overset{?}{=} đQ - \underbrace{đW}_{\substack{\text{work} \\ \| \\ 0}} = T dS$

$$dS = \frac{1}{T} dU, \quad T \text{ const, so } \int dS = \int dU = 0$$
$$\Delta S \overset{?}{=} 0$$

A. $dU = T dS$ assumes a reversible process, which this is not.

66

blank

(67)

2/17/23 Fri.:
1. isothermal
2. adiabatic
3. isobaric
} reversible processes
4. irreversible

today: example
metals

Wed.: metals, neutron stars

MIDTERM: Mon. 3/3 — one 8.5×11" sheet handwritten both sides; no calculators (won't be useful anyway)

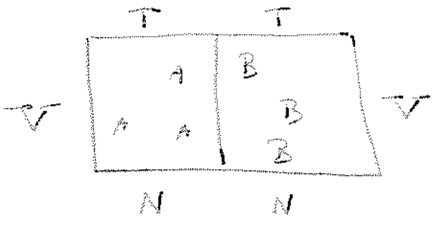
Some further comments on reversible processes of an ideal gas:

1) Where we had to heat the system externally (as in the isobaric expansion), it's important that the reservoir should be no more than infinitesimally different in T from the system, or the process will be inherently irreversible.
2) We're not limited to the processes outlined; any curve in the PV plane corresponds to some reversible process.
3) However, just because we can draw a PV curve does not mean that a given process is reversible.

ex 6-6. $\boxed{\text{READ}}$

[already specified] ~~To get the result K&K want, we have to assume additionally that the two gases are at the same pressure, i.e., $V_A = V_B$~~

before



$n_Q^A \neq n_Q^B$ in general because masses may differ

"start" so monatomic

before $S = S_A + S_B = Nk_B\left[\ln\left(\frac{n_Q^A}{n}\right) + \ln\left(\frac{n_Q^B}{n}\right) + 5\right]$, $n = N/V$ (same for A & B)

after $S' = S_A' + S_B' = Nk_B\left[\ln\left(\frac{n_Q^A}{n'}\right) + \ln\left(\frac{n_Q^B}{n'}\right) + 5\right]$, $n' = \frac{N}{2V}$

$$\Delta S = S' - S = 2Nk_B \ln\left(\frac{n}{n'}\right) = \boxed{2Nk_B \ln 2}$$

(68)

Paradox: What if A = B? Clearly no change in entropy, since we were already in equilibrium before, yet calc. shows $\Delta S \neq 0$.
Sol'n, as we've seen before, is to correct for "indistinguishable" particles.

Before: $Z = Z_A Z_B = \left[\frac{(n_Q V)^N}{N!}\right]^2$

$$F = -k_B T \ln Z$$
$$= -2 k_B T \left[N \ln(n_Q V) \overbrace{- N \ln N + N}^{\text{stirling}}\right]$$

$$= -2 N k_B T \left[\ln(n_Q V) - \ln N + 1\right]$$ extensive, as shown on a HW

after: $Z' = (2 n_Q V)^{2N} / (2N)!$

$$F' = -N k_B T \left[2 \ln(2 n_Q V) - 2 \ln(2N) + 2\right]$$

$$= -2 N k_B T \left[\ln(n_Q V) + \ln 2 - \ln 2 - \ln N + 1\right] = F.$$

Since $S = -\left(\frac{\partial F}{\partial T}\right)_V$, $\Delta S = 0$.

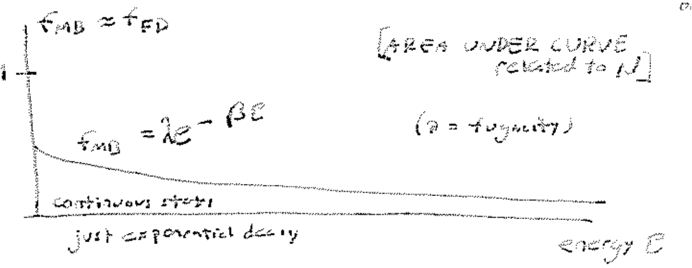
What determines the "typical" energy scale in a Fermi gas?

Classically, the only energy scale is $k_B T$.

In QM, the density, n, controls the energy scale: if $n \gg n_Q(T)$, e^- must go to very high-energy states, because there aren't enough low-energy ones.

classical: $n \ll n_Q$, so $\mu = k_B T \ln(n/n_Q) < 0$. Then $e^{(\varepsilon-\mu)\beta} \gg 1$, so $f_{MB} \approx f_{FD}$.

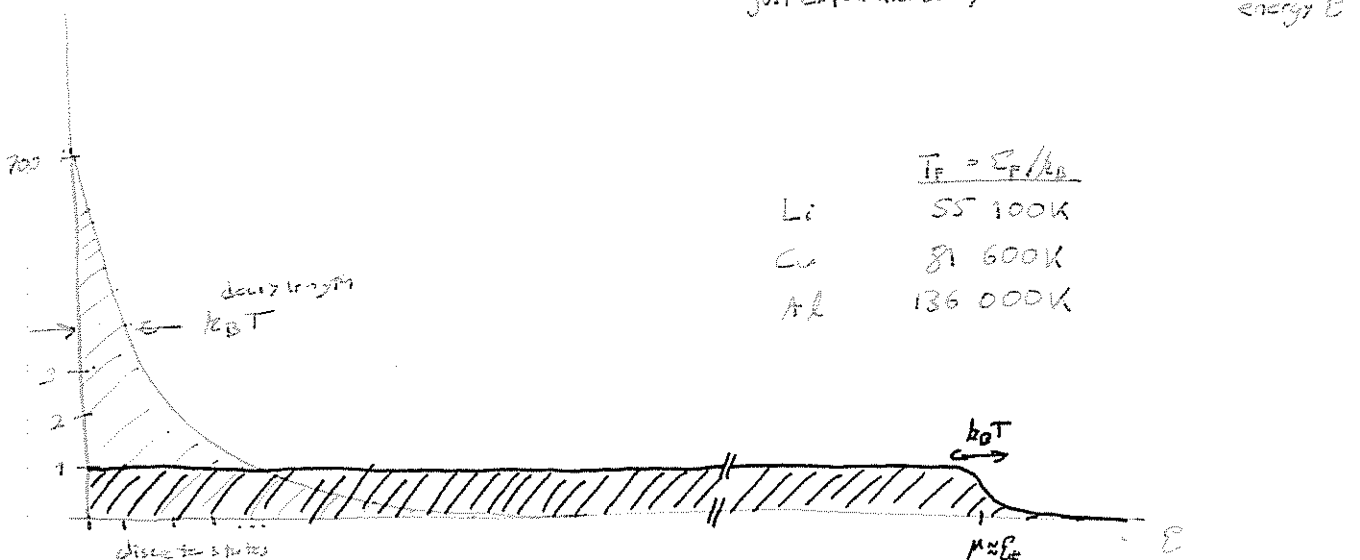
Schematics: non-degenerate (classical)



[AREA UNDER CURVE related to N]

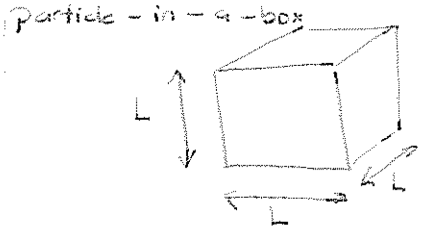
(λ = fugacity)

degenerate:

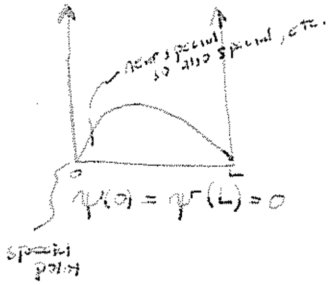


	$T_F = \varepsilon_F / k_B$
Li	55 100K
Cu	81 600K
Al	136 000K

particle-in-a-box



boundary conds.:



$\psi(0) = \psi(L) = 0$

Eigenstates are standing waves: no good for transport

Born-von Karman (periodic) boundary conditions

$\psi(x+L, y, z) = \psi(x, y, z)$

etc.

This periodicity has nothing to do w/ underlying atomic structure ($L \gg a$): it is there only to let us do particle-in-a-box without the box. You may think of L as a sample size, although we're going to take $\lim_{L\to\infty}$.

No special points:

Sol'n to time-ind. SE: $\psi_{\vec{k}}(\vec{r}) = \underbrace{\frac{1}{L^{3/2}}}_{\text{normaliz'n}} e^{i\vec{k}\cdot\vec{r}}$

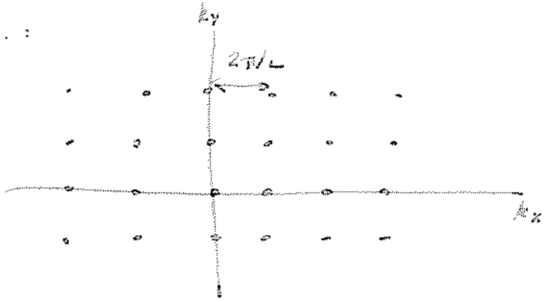
Since momentum $\hat{p} = -i\hbar\vec{\nabla}$, $\vec{p} = \hbar\vec{k}$ for free wave

b.c. $\Rightarrow \quad e^{ik_xL} = e^{ik_yL} = e^{ik_zL} = 1$

$$\Rightarrow k_j = \frac{2\pi n_j}{L}, \quad j = x, y, z, \quad n_j = \pm 0, 1, 2, \ldots$$

are as in K&K; conventional to use the k_j as fundamental

In 2 dims.:



This discretization is artificial, since it depends on sample size (L). We're really interested in density of levels in k space.

A region of k space with volume $M \times M \times M$  contains $\left(\frac{M}{2\pi/L}\right)^3$ levels, Problem 7.$\overset{1}{2}$: DOS in 1 & 2 dims.

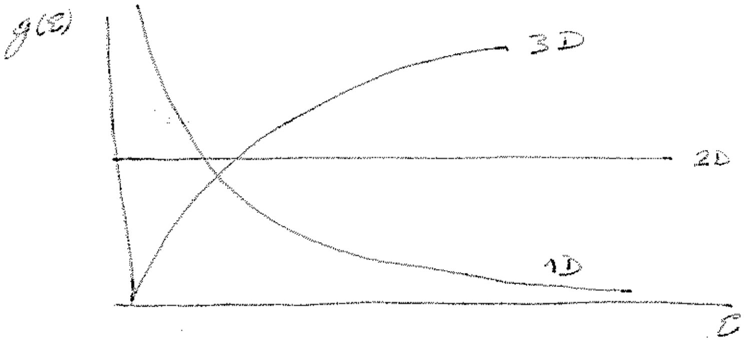
2D: could do it same way; here's an equivalent.

total # states per unit ~~volume~~ area with $k \leq k_0 \equiv \nu = \overset{\text{spin}}{2}\,\frac{\pi k_0^2}{4\pi^2} = \frac{k_0^2}{2\pi} = \frac{m\mathcal{E}}{\pi\hbar^2}$ where $\mathcal{E} = \frac{\hbar^2 k_0^2}{2m}$

$$g(\mathcal{E}) = \frac{d\nu}{d\mathcal{E}} = \boxed{\frac{m}{\pi\hbar^2}}$$

1D: $\nu = 2 \cdot \frac{2k_0}{2\pi} = \frac{2k_0}{\pi} = \frac{2\sqrt{2m\mathcal{E}}}{\pi\hbar}$

$$\frac{d\nu}{d\mathcal{E}} = \frac{1}{2} \cdot \frac{2}{\pi\hbar}\sqrt{\frac{2m}{\mathcal{E}}} = \boxed{\frac{1}{\pi\hbar}\sqrt{\frac{2m}{\mathcal{E}}}}$$



1D: energy levels get sparse at high energy since $\mathcal{E} \propto k^2$

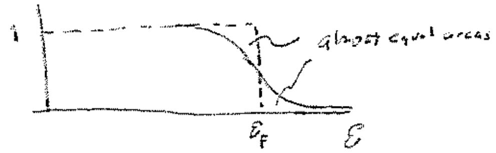
3D: more k-volume far out, so more levels

2D: effects exactly cancel

Implications for dep. of chem. pot. on T at low T:

need $n = \frac{N}{V} = \text{const.} = \int_0^\infty d\mathcal{E}\, f_T(\mathcal{E})\, g(\mathcal{E})$

$f(\mathcal{E})$:



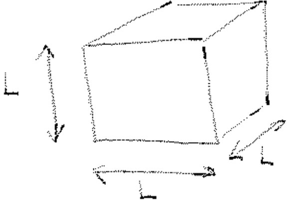
3D: since $g \uparrow$ as $\mathcal{E}\uparrow$, we must shift $\mu \downarrow$; otherwise, triangle above μ times $g(\mathcal{E} > \mu)$ has more states than one below times $g(\mathcal{E} < \mu)$

result: $\mu = \mathcal{E}_F - \mathcal{O}\left(\frac{T}{T_F}\right)^2 \mathcal{E}_F$

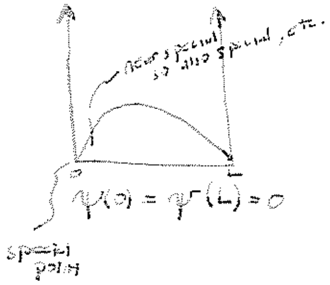
1D: $g \downarrow$ as $\mathcal{E}\uparrow$, so $\mu \uparrow$

references : AGM ch2, app. C
Pathria app. E

particle-in-a-box



boundary conds.:



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Born-von Karman (periodic) boundary conditions

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etc.

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No special points:

Sol'n to time-ind. SE: $\psi_{\vec{k}}(\vec{r}) = \underbrace{\frac{1}{L^{3/2}}}_{\text{normaliz'n}} e^{i\vec{k}\cdot\vec{r}}$

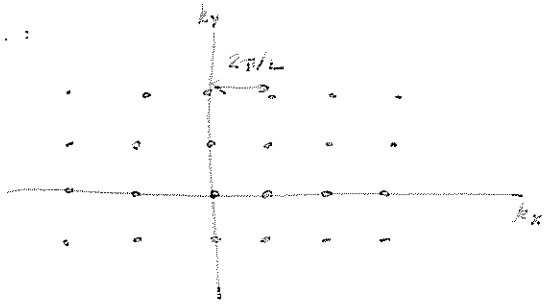
Since momentum $\hat{p} = -i\hbar\vec{\nabla}$, $\vec{p} = \hbar\vec{k}$ for free wave

b.c. $\Rightarrow$ $e^{ik_xL} = e^{ik_yL} = e^{ik_zL} = 1$

$$\Rightarrow k_j = \frac{2\pi n_j}{L}, \quad j = x, y, z, \quad n_j = \pm 0, 1, 2, \ldots$$

are as in KOK; conventional to use the k_j as fundamental

In 2 dims.:



This discretization is artificial, since it depends on sample size (L). We're really interested in density of levels in k space.

A region of k space with volume $M \times M \times M$  contains $\left(\frac{M}{2\pi/L}\right)^3$ levels,

(70)

So density of levels in k space $= \frac{L^3}{8\pi^3} = \frac{V}{8\pi^3}$ (V = volume of sample)

Energy $\mathcal{E} = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$

Surface of constant $\mathcal{E}$ in k space is a sphere

At $T=0$, all states (dots) inside some sphere will be occupied, all outside unoccupied. (radius $\equiv k_F$)

2/17/03 ?

We fill dots up two at a time (spin ↑, ↓). How far out do we get in k space?

Density of e^-'s $= n = N/V$:

$$\underbrace{2}_{\text{spin}} \cdot \underbrace{\frac{4\pi k_F^3}{3}}_{\substack{\text{volume in} \\ k \text{ space}}} \cdot \underbrace{\frac{V}{8\pi^3}}_{\substack{\text{density of levels} \\ \text{in } k \text{ space}}} = nV = N$$

$$\boxed{k_F^3 = 3n\pi^2}$$

V (L) has dropped out.

Related measures:

$\mathcal{E}_F = \frac{\hbar^2 k_F^2}{2m} \sim 1.5 - 15\text{ eV}$ for a typical metal

$T_F = \mathcal{E}_F / k_B \sim 10^4 - 10^5\text{ K}$

$v_F = p_F/m = \frac{\hbar k_F}{m} \sim 10^8\text{ cm/s} \sim 0.01c$

accurate band-structure calcs. include relativistic effects

NOT same as drift velocity (which is much slower) or propagation speed of a disturbance (which is even faster)

At $T=0$, $\mu = \frac{\hbar^2 k_F^2}{2m} = \mathcal{E}_F$. At $T>0$, chemical potential set by

$$\int d^3k \, \frac{V}{8\pi^3} \, \overset{\text{spin}}{2} f_{FD}(\mathcal{E}(\vec{k})) = N \qquad \text{where} \qquad f_{FD}(\mathcal{E}) = \cancel{\frac{\overset{\text{exp}}{e}^{-(\mathcal{E}-\mu)\beta}}{Z}} \quad \text{(Fermi-Dirac)}$$

$$\text{or} \quad \boxed{\int d^3k \cdot \frac{1}{4\pi^3} f_{FD}(\mathcal{E}(\vec{k})) = n} \qquad\qquad = \frac{1}{e^{(\mathcal{E}-\mu)\beta}+1}$$

This integral is most easily evaluated for free electrons by changing the integration variable from $\vec{k}$ to $\mathcal{E}$, which depends only on the magnitude of k.

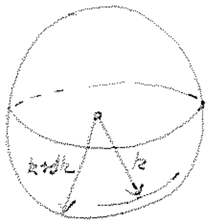
71

$$\boxed{n = \int g(\mathcal{E})\, f_{FD}(\mathcal{E})\, d\mathcal{E}}$$

where $g(\mathcal{E})\,d\mathcal{E}$ is the density of levels with energies between $\mathcal{E}$ and $\mathcal{E}+d\mathcal{E}$.
(K&K use $\frac{\mathcal{D}(\mathcal{E})}{V}$, but that's harder to write)

i.e. # levels per energy per unit volume of material

Calculate $g(\mathcal{E})$ in 3 dims.:



Volume of spherical shell in k space is $\frac{4\pi}{3}\left[(k+dk)^3 - k^3\right]$

$$= 4\pi k^2 dk + \mathcal{O}(dk)^2 .$$

It contains (per unit sample volume, V):

$$\underbrace{2}_{\text{spin}} \cdot \underbrace{\frac{1}{8\pi^3}}_{\substack{\text{density of}\\ k \text{ levels}}} \cdot \underbrace{4\pi k^2 dk}_{\substack{\text{volume}\\ \text{of shell}}} = \boxed{\frac{k^2}{\pi^2}\, dk}$$

states
levels, all at energy $\mathcal{E} = \frac{\hbar^2 k^2}{2m}$

$\downarrow$ below, set $= g(\mathcal{E})\,d\mathcal{E}$

$$\boxed{\frac{k^2}{\pi^2} dk = g(\mathcal{E})\, d\mathcal{E}}$$

Eliminate dk from l.h.s.: $k = \frac{1}{\hbar}\sqrt{2m\mathcal{E}}$, so $dk = \frac{2m}{\hbar}(2m\mathcal{E})^{-1/2}\, d\mathcal{E}$

$$= \frac{m\, d\mathcal{E}}{\hbar\sqrt{2m\mathcal{E}}}$$

So $$g(\mathcal{E})\,d\mathcal{E} = \frac{k^2}{\pi^2}\,\frac{m\,d\mathcal{E}}{\hbar^2\sqrt{2m\mathcal{E}}}$$

$$= \frac{2m\mathcal{E}}{\hbar^2 \pi^2}\,\frac{m\,d\mathcal{E}}{\hbar^2\sqrt{2m\mathcal{E}}} = \boxed{\frac{m\sqrt{2m\mathcal{E}}}{\hbar^3\,\pi^2}}\, d\mathcal{E} \quad \text{for } \mathcal{E} \geq 0$$

2/19/03 Monday: Classical entropy of mixing
Fermi gas: density of one-particle levels in k space
Today: metals, neutron stars
Fri.: Bosons

finish pp 70-1

Problem $7.\overset{1}{2}$: DOS in 1 & 2 dims.

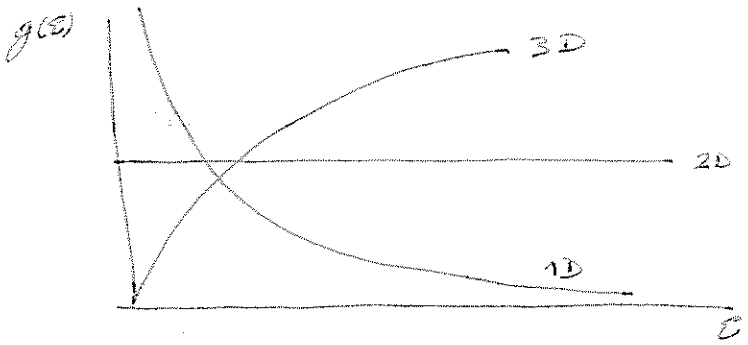
2D: could do it same way; here's an equivalent.

total # states per unit $\overset{\text{area}}{\text{volume}}$ with $k \le k_0 \equiv \nu = \overset{\text{spin}}{2}\,\frac{\pi k_0^2}{4\pi^2} = \frac{k_0^2}{2\pi} = \frac{m\mathcal{E}}{\pi\hbar^2}$ where $\mathcal{E} = \frac{\hbar^2 k_0^2}{2m}$

$$g(\mathcal{E}) = \frac{d\nu}{d\mathcal{E}} = \boxed{\frac{m}{\pi\hbar^2}}$$

1D: $\nu = 2 \cdot \frac{2k_0}{2\pi} = \frac{2k_0}{\pi} = \frac{2\sqrt{2m\mathcal{E}}}{\pi\hbar}$

$$\frac{d\nu}{d\mathcal{E}} = \frac{1}{2} \cdot \frac{2}{\pi\hbar}\sqrt{\frac{2m}{\mathcal{E}}} = \boxed{\frac{1}{\pi\hbar}\sqrt{\frac{2m}{\mathcal{E}}}}$$



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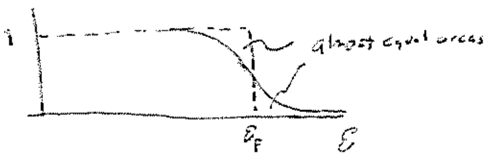
3D: more k-volume far out, so more levels

2D: effects exactly cancel

Implications for dep. of chem. pot. on T at low T :

need $n = \frac{N}{V} = \text{const.} = \int_0^\infty d\mathcal{E}\, f_T(\mathcal{E})\, g(\mathcal{E})$

$f(\mathcal{E})$:



3D: since $g \uparrow$ as $\mathcal{E}\uparrow$, we must shift $\mu \downarrow$; otherwise, triangle above μ <u>times</u> $g(\mathcal{E} > \mu)$ has more states than one below <u>times</u> $g(\mathcal{E} < \mu)$

result: $\mu = \mathcal{E}_F - \mathcal{O}\left(\frac{T}{T_F}\right)^2 \mathcal{E}_F$

1D: $g \downarrow$ as $\mathcal{E}\uparrow$, so $\mu \uparrow$

references : A&M ch2, app. C

Pathria app. E

Heat capacity of metals:

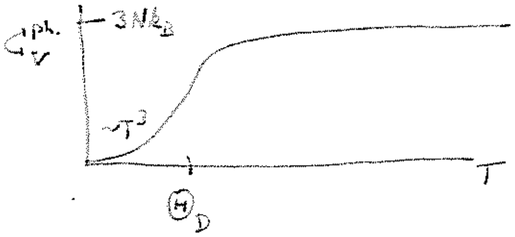
1. Why does du Long-Petit work so well $\overset{\text{at high } T}{\wedge}$ when it ignores conduction e^-s? ← which should contribute additional $\sim\frac{3}{2}N_e k_B$

   $(3Nk_B)$

2. Why is C_V much bigger at very low T than the $\sim T^3$ predicted by the phonon theory at low T?

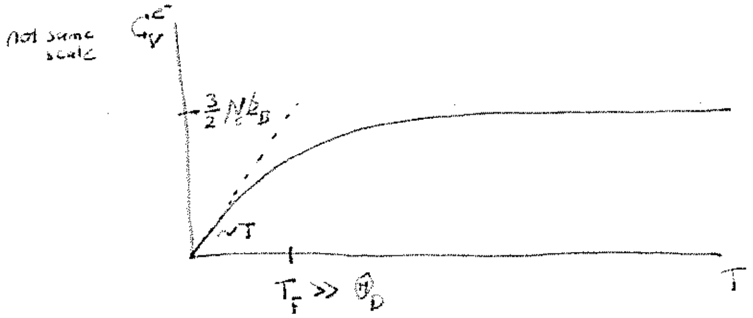
[illegible]

Recall phonon theory:



[better drawn next]

answer:



N_e = # conduction e^-s

Answers to puzzles:

1) At $\Theta_D \lesssim T \ll T_F$, $3Nk_B \gg C_V^{e^-}$

2) At $T \ll \Theta_D$, linear in T wins out over $\sim T^3$ $(C_V^{e^-} \gg C_V^{ph})$

[illegible]

$$\boxed{T \ll T_F}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} = \frac{d\beta}{dT}\left(\frac{\partial U}{\partial \beta}\right)_{V,N} = -\frac{1}{k_B T^2}\left(\frac{\partial U}{\partial \beta}\right)_{V,N}$$

$$U(T) = V\int_0^\infty d\mathcal{E}\ \mathcal{E}\ g(\mathcal{E})\ \underbrace{f(\beta,\mathcal{E})}$$

1. only $\underset{(T)}{\beta}$ dependence, through both β and μ → 2nd order in β (or T) Sommerfeld

$$f(\beta,\mathcal{E}) = \frac{1}{e^{(\mathcal{E}-\mu)\beta}+1}$$

2. K&K do some acrobatics to put $\mathcal{E}-\mathcal{E}_F$ here instead of $\mathcal{E}$ — comes down to arbitrary choice of origin (complicated by limit on integral)

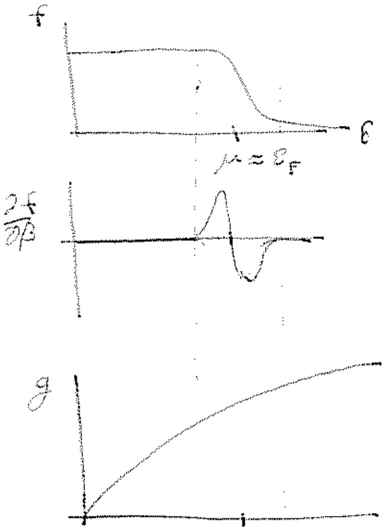
Acrobatics correct but unnecessary

4/11/13

$$\frac{C_V}{V} = -\frac{1}{k_B T^2}\int_0^\infty d\varepsilon\ \varepsilon\ \underbrace{g(\varepsilon)}\ \underbrace{\frac{\partial f(\beta,\varepsilon)}{\partial \beta}}$$

non zero only within $\sim k_B T$ of μ, varies rapidly

varies slowly by comparison, so take out at ε_F



Set $\mu \approx \varepsilon_F \quad (-\mathcal{O}(T/T_F)^2\varepsilon_F)$

$$\frac{C_V}{V} \approx -\frac{g(\varepsilon_F)}{k_B T^2}\int_0^\infty d\varepsilon\ \varepsilon\ (-1)\left[e^{(\varepsilon-\varepsilon_F)\beta}+1\right]^{-2}\left(\varepsilon-\varepsilon_F-\beta\frac{\partial\mu}{\partial\beta}\right)e^{(\varepsilon-\varepsilon_F)\beta}$$

second order, so ignore

Let $x = (\varepsilon-\varepsilon_F)\beta$ $\qquad \varepsilon = k_B T x + \varepsilon_F$

$$\frac{C_V}{V} \approx \frac{g(\varepsilon_F)}{k_B T^2}\int_{-\varepsilon_F\beta}^{\infty} k_B T\, dx\ (k_B T x + \varepsilon_F)\left[e^x+1\right]^{-2} k_B T x\, e^x$$

$$= g(\varepsilon_F)\, k_B \int_{-\varepsilon_F\beta}^{\infty}\frac{(k_B T x^2 + \varepsilon_F x)e^x}{(e^x+1)^2}dx$$

tiny for $x \lesssim -\varepsilon_F\beta$ since $\varepsilon_F\beta \gg 1$

$$\approx k_B\, g(\varepsilon_F)\left[k_B T\int_{-\infty}^{\infty}\frac{x^2 e^x}{(e^x+1)^2}dx + \varepsilon_F\int_{-\infty}^{\infty}\frac{x e^x\, dx}{(e^x+1)^2}\right]$$

second integrand

$$= \frac{x e^x}{(e^x+1)^2}\,\frac{e^{-x}}{e^{-x}} = \frac{x}{(e^{x/2}+e^{-x/2})^2}$$ odd, so integral vanishes

first integral : BOOK → $\pi^2/3$

2/21/03 Wed: DOS $g(\mathcal{E}) = \frac{m\sqrt{2m\mathcal{E}}}{\hbar^3 \pi^2}$ (3D)

today: finish C_V calc. for degenerate Fermi gas
start Bose gas
Mon.: superfluidity

---

setup p73, p74

$$\frac{C_V}{V} = \frac{1}{3}\pi^2 g(\mathcal{E}_F) k_B^2 T$$

$$g(\mathcal{E}_F) = \frac{m\sqrt{2m\mathcal{E}_F}}{\hbar^3 \pi^2} = \frac{m\,\mathcal{E}_F^{3/2}\sqrt{2m}}{\hbar^3\pi^2\,\mathcal{E}_F}$$ will be convenient below

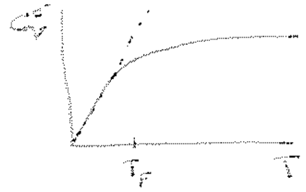
To get $\mathcal{E}_F$ in terms of n (number density), fix at zero temp.:

$$n = \frac{N}{V} = \int_0^\infty g(\mathcal{E}) f(T=0,\mathcal{E})\,d\mathcal{E} = \int_0^{\mathcal{E}_F} g(\mathcal{E})\,d\mathcal{E} = \int_0^{\mathcal{E}_F} \frac{m\sqrt{2m\mathcal{E}}}{\hbar^3\pi^2}\,d\mathcal{E} = \frac{m^{3/2}\sqrt{2}}{\hbar^3\pi^2}\,\frac{2}{3}\mathcal{E}_F^{3/2}$$

$$\text{or } \mathcal{E}_F^{3/2} = \frac{3}{2}\,n\,\frac{\hbar^3\pi^2}{m^{3/2}\sqrt{2}}$$

$$\text{so } g(\mathcal{E}_F) = \frac{m\sqrt{2m}}{\hbar^3\pi^2}\cdot\frac{1}{\mathcal{E}_F}\cdot\frac{3}{2}\,n\,\frac{\hbar^3\pi^2}{m^{3/2}\sqrt{2}} = \frac{3}{2}\frac{n}{\mathcal{E}_F} = \boxed{\frac{3}{2}\frac{n}{k_B T_F}}$$

Thus the volumetric specific heat $\frac{C_V^{el}}{V} = \boxed{\frac{1}{2}\pi^2 n k_B \frac{T}{T_F}}$ for $T \ll T_F$



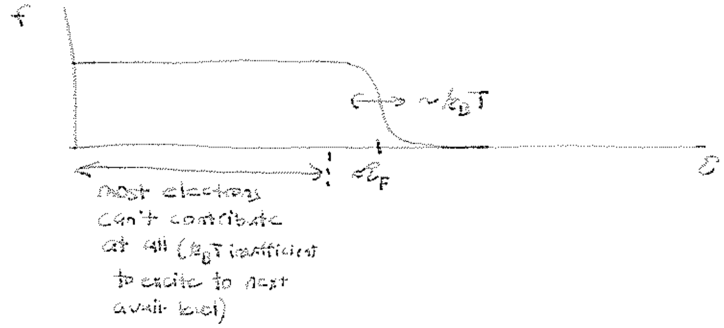
The results are good for some metals, not so good for others. Since $T_F = T_F(m)$, we can fudge the bad results by replacing $m \to m^*$

Metal	m^*/m
Ag	1.1
Au	1.1
K	1.2
Na	1.3
Nb	12
Mn	27
Bi	0.047

Main source of discrepancy, surprisingly, not neglected e^--e^- interaction so much as neglected lattice periodicity:

1) Fermi surface not necessarily spherical
2) band effective mass m^* ($\neq m^*_{cv}$)
$$\mathcal{E} \approx \frac{\hbar^2 k^2}{2m^*}$$

Physically-plausible argument for the linear C_V:

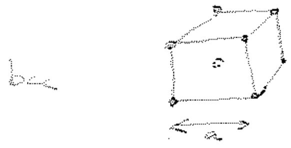


$$\begin{aligned}
\#\, e^-\text{s} \quad &= \quad N \\
\text{fraction that \underline{can} contribute} \quad &\simeq \quad k_B T/\mathcal{E}_F \\
\text{"equipartition"} \quad &\rightarrow \quad \tfrac{1}{2}\, k_B T \\
\hline
U \quad &\simeq \quad \tfrac{N}{2}\,(k_B T)^2/\mathcal{E}_F
\end{aligned}$$

$$C_V \quad \simeq \quad N k_B^2\, T/\mathcal{E}_F \quad = \quad N k_B\,(T/T_F)$$ misses only the factor $\pi^2/2$

Estimate T_F for a monovalent free-e^- metal:

<u>Na</u> lattice constant $a = 4.23\ \text{Å}$



1 valence e^- per Na, so # density of atoms = # density of e^-s:

$$n = \frac{\frac{1}{8}\cdot 8 + 1}{a^3} = \frac{2}{a^3} = 2.6\cdot 10^{22}\ \text{cm}^{-3}$$

$$T_F = \frac{\mathcal{E}_F}{k_B} = \frac{1}{k_B}\left(\frac{3}{2}\, n\, \frac{\hbar^3 \pi^2}{m^{3/2}\sqrt{2}}\right)^{2/3} = 37\,000\ \text{K}$$

Some other Fermi gases:

e^- in white-dwarf star $\quad T_F \sim 3\cdot 10^9\,\text{K}$

$T \sim 10^7\,\text{K}$ so again, from the e^-'s point of view, a white dwarf is very cold ($\rightarrow$ degenerate Fermi gas)

p.s. [KGK show that $mc^2 \sim \frac{1}{2} m v^2$ so really should ~~[illegible]~~ replace latter with relativistic version $c^2 M$?

(77)

Neutron star: n, p^+ are Fermions
(really a quark-gluon soup, but n-like and p-like quasiparticles)

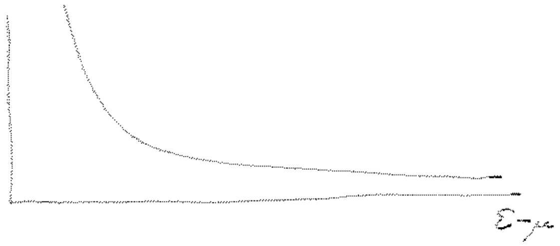
$T_F \sim 3\cdot10^{11}\,K$

Lecture 8 2/20/[illegible] 2/23/05

I should offer examples of non-degenerate Fermi gases: e^-'s in semiconductors (doped or undoped, T), ^{129}Xe or ^{131}Xe, etc. [illegible] Fermi gas at [illegible]

Bose gas - N Bosons (e.g. ^4He atoms - $2p^+, 2n, 2e^-$ ea.)

$$f_{BE}(T,\mathcal{E}) = \frac{1}{e^{(\mathcal{E}-\mu)\beta}-1}$$



At any temp., $\mu \overset{must}{<} \mathcal{E}_{ground}$ to avoid blow-up + neg. occ. #

w.o.l.og., set $\mathcal{E}_{ground}=0$, so $\mu<0$.

For Bose gas at low T, we cannot replace the sum over states with an integral over a D.O.S., since as the graph shows, occupation of low-energy states may be significant.

$$N = \sum_{\substack{\lambda\\ states}} f_{BE}(T,\mathcal{E}_\lambda)$$

At $T=0$ exactly, μ must be such that $f_{BE}(0,\mathcal{E}_\lambda) = \begin{cases} N & \text{for } \mathcal{E}_\lambda=0 \\ 0 & \text{for } \mathcal{E}_\lambda>0 \end{cases}$

We can't evaluate f_{BE} directly at $T=0$, so we take a limit:

$$N \equiv \lim_{T\to0} f_{BE}(T,\mathcal{E}=0) = \lim_{T\to0}\frac{1}{e^{-\mu\beta}-1} \quad ; \quad 0<-\mu\beta\ll1$$

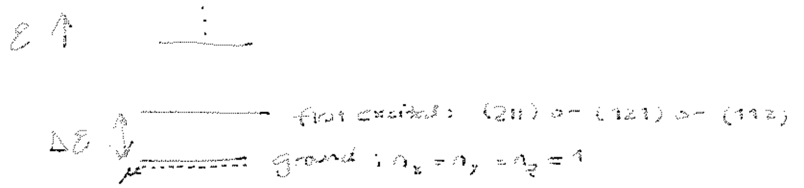
equal to first order as $T\to0$ only afterward

$$= \lim_{T\to0}\frac{1}{(1-\mu\beta+\frac{1}{2}[\mu\beta]^2-\dots)-1} \doteq -\lim_{T\to0}\frac{k_BT}{\mu} - \mathcal{O}\left(\frac{\mu}{k_BT}\right)^2$$

So in limit, $\mu = -\frac{k_BT}{N} - \mathcal{O}\left(\frac{1}{N}\right)^2$

Difference between BE & MB at very low T:

particle in a box $\mathcal{E} = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 (n_x^2 + n_y^2 + n_z^2)$, $n_x, n_y, n_z \geq 1$



μ infinitesimally (negative) below zero

play in L = 1cm, m = mass of ⁴He

$$\Delta\mathcal{E} = 3\cdot10^{-30}\,\text{erg} = \frac{1}{k_B}\cdot2\cdot10^{-14}\,\text{K}$$

For convenience set $\mathcal{E}_{ground} = 0$. Set $T = 1\,\text{mK} \gg \frac{\Delta\mathcal{E}}{k_B}$, so energy spacing doesn't appear important, classically

$n \sim 10^{22}/\text{cm}^3$

$\beta = 0.724\cdot10^{19}\,\text{erg}^{-1}$ $k_BT = 1.381\cdot10^{-19}\,\text{erg}$

$\mu = \frac{k_BT}{N} \sim -1.4\cdot10^{-41}\,\text{erg}$

[illegible] paradox

μ cancels, is defined as Paradox of this

$$\frac{\text{occ. } \cancel{\text{prob}}\text{(ground)}}{\text{occ. } \cancel{\text{prob}}\text{ (1}^{\text{st}}\text{ excited)}} = ① \text{ Boltzmann: } \frac{\lambda e^{0}}{\lambda e^{-\Delta\mathcal{E}\beta}} \approx \frac{1}{\exp(-2\cdot10^{-11})}$$

$$\approx \frac{1}{1 - 2\cdot10^{-11}} \approx 1 + 2\cdot10^{-11} \approx 1$$

ground and first excited state equally occupied

$$② \text{ Quantum: } \frac{\exp[(\Delta\mathcal{E} - \mu)\beta] - 1}{\exp[-\mu\beta] - 1}$$

$$= \frac{\exp[(3\cdot10^{-30}\,\text{erg} + 1.4\cdot10^{-41}\,\text{erg})\cdot0.72\cdot10^{19}\,\text{erg}^{-1}] - 1}{\exp[1.4\cdot10^{-41}\,\text{erg}\cdot0.72\cdot10^{19}\,\text{erg}^{-1}] - 1}$$

$$= \frac{e^{2\cdot10^{-11}} - 1}{e^{10^{-22}} - 1} \overset{\text{Taylor}}{=} \frac{2\cdot10^{-11}}{10^{-22}} = 2\cdot10^{11}$$

So the first excited state isn't very important.

In fact, at this temp, only the ground state matters (despite $k_BT \gg \Delta\mathcal{E}$).

2/24/03 last week: degenerate Fermi gas
today: degenerate Bose gas
interactions → superfluidity
Wed.: superfluidity
review

pp. 77-78

Number in ground $N_0 = \frac{1}{e^{-\mu\beta}-1} = \frac{1}{\lambda^{-1}-1}$

occupation of <u>all</u> excited states — justified using an integral (rather than a sum) because nothing special in ratio of 2nd excited to 1st excited (μ far away from both → no tiny denominators as on p. 78)

in all excited states $N_e = V\int_0^\infty d\varepsilon\, g(\varepsilon) f_{BE}(\varepsilon)$ same $g(\varepsilon)$ as for e^- gas

Note: this misses the ground state, since in 3D $g(0)=0$.

$$N_e \overset{\text{book}}{=} \underbrace{\zeta\left(\tfrac{3}{2}\right)}_{2.61238} n_Q V$$

<u>IF</u> $\lambda = e^{+\mu\beta} \approx 1$

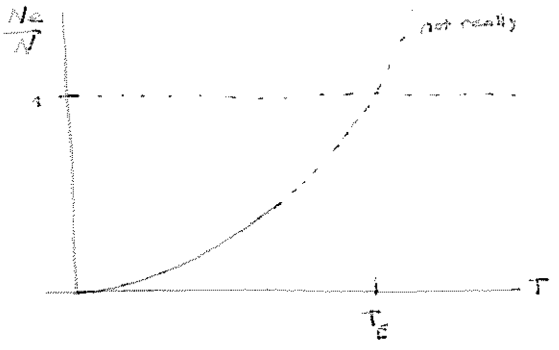
Same approx'n as $\mu \approx -\frac{k_B T}{N}$ $\left(+\mathcal{O}(T/T_{\text{something}})^2\right)$

$\lambda = e^{\mu\beta} = e^{-1/N} \approx 1$

$$\equiv \zeta\left(\tfrac{3}{2}\right)\cdot \overset{\text{constant}}{C}\cdot T^{3/2}\, V \qquad C = \left(\frac{M k_B}{2\pi\hbar^2}\right)^{3/2}$$

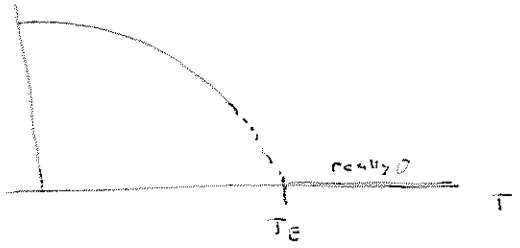
$$\equiv (T/T_E)^{3/2}\, N \quad \text{where} \quad T_E = \left[\frac{N}{CV\,\zeta(3/2)}\right]^{2/3}$$

fraction in excited states $\frac{N_e}{N}$



T_E is the temp. scale for which $\mu \approx -\frac{k_B T}{N} - \mathcal{O}(T^2/T_E)$, so the approx'n breaks down for $T \gtrsim T_E$.

fraction in ground state $1 - \frac{N_c}{N}$

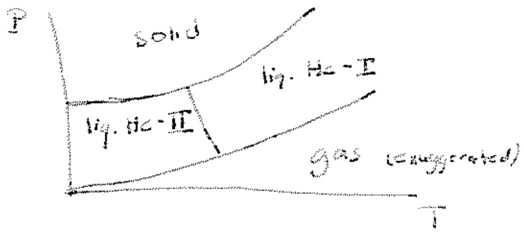


Phenomenology of ^{4}He

- interactions strong, so not a gas but a liquid

However, for some purposes gas model still good

1.



self-respecting substances do not stay liquid down to $T=0$, but ^{4}He does

"3rd law" = unique groundstate (or at least # ground states grows more slowly than e^N)

Suggests ^{4}He is a <u>perfectly</u> <u>ordered</u> fluid (unlike any normal liquid)

2. Appearance going through transition (cooling $\overset{\text{evaporative}}{}$)

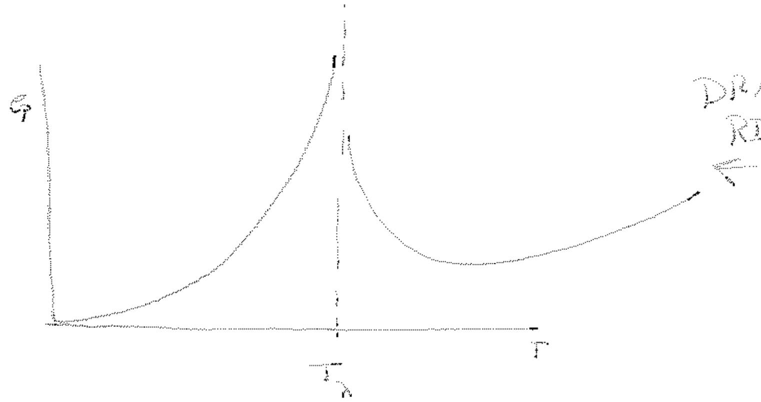
clear fluid above & below crit temp

but no visible boiling below

⟵ excellent thermal conductivity

(heat conducted ballistically instead of diffusively, so technically $\kappa = \infty$)

3. specific heat



DRAW FROM RIGHT

"λ" because it looks like Λ. $T_\lambda \approx T_E$

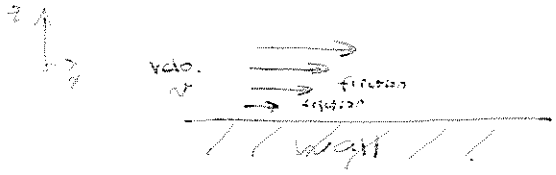
Divergent specific heat characteristic of a 2nd order phase transition

One with an order parameter that's zero on the high-T side & goes continuously to zero on the low-T side.

2/23/04
2/14/03

4. Physicists do not abuse the term "super" ≠ very
= beyond, on top of

flow of a normal fluid in a tube



drag force per unit area $= \eta \frac{\partial v_x}{\partial z}$

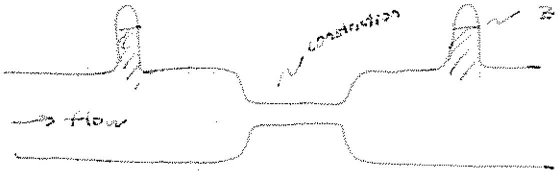
η viscosity

Sample viscosities (laminar flow)

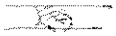
		η		
linseed oil	30°C	33 poise	$\left(= \frac{\text{dyne sec}}{\text{cm}^2}\right)$	
water	30°C	$8.01 \cdot 10^{-3}$		
air	20°C	$1.81 \cdot 10^{-4}$		
^{4}He-II	<2.7K	0	$(< 10^{-9}$ poise$)$ Kapitza 1937	$< 10^{-11}$ poise Kapitza 1941 see RMP 26, 192 (1954)

exact: $\vec{\nabla} \times \vec{v} = 0$ so $\frac{\partial v_x}{\partial z} = 0 \Rightarrow$ no drag force

Some evidence



zero loss in pressure so long as $v < v_c$

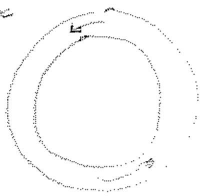
push powder into tube  so normal fluid can't get through

$T > T_\lambda$: nothing gets through

$T < T_\lambda$: no loss in pressure (no impediment to flow)

Talk about superleaks in expt'l physics

Gyroscope

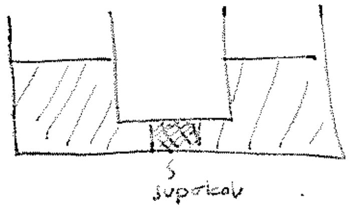


Start flow in tube $T > T_\lambda$. Cool down below T_λ. Stop rotation: how long does fluid continue to flow (until you [illegible])? Forever. (Longer than experimenters willing to wait.)

added: weirdness : T↑ (but $< T_\lambda$) : ang. mom. decreases (torque!)
T↓ to orig. : original ang. mom. restored.

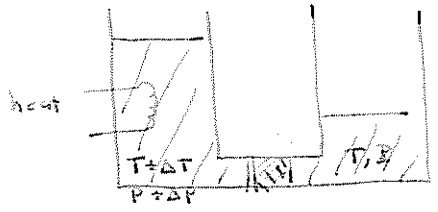
Apparently $\vec{v}$ stays constant, only mass (fraction of participating helium) changes.

5.



before

"fountain effect"



during & after - stays this way so long as normal component cannot go through superleak

opposite also true: if fluid forced right → left, left side will be warmer (not Peltier, which is a small effect and irreversible — this effect is large & reversible).

6. Supersiphon

Capillary height very great because He would rather be next to just about anything other than He ("universal wetter"); no loss due to friction, because there isn't any.

7. $\vec{\nabla} \times \vec{v} = 0$: ∴ if we try to rotate, get vortices of normal fluid (quantized) - this and fountain effect show that superfluidity not merely perfect (frictionless) fluidity but goes beyond that.

2/26/03

Mon.: Bose gas
today: Superfluid (already showed 1. phase diagram 2. appearance 3. 4tr)
review
Fri. review

pp 82-3

Two-fluid model: normal component and superfluid component.
Entropy of latter = 0.

most striking aspect of s.f. is lack of friction in flow - Origin:

For friction, we need a collision between wall & s.f. creating an excited state in latter. Convenient to work in rest frame of s.f., so we have

	wall		superfluid	
	before	after	before	after
momentum	$\vec{P}$	$\vec{P}'$	0	$\hbar\vec{k}$
energy	E	E'	0	$\mathcal{E}$

initial wall velocity: $\vec{v}$
mass M

$$\vec{P}' = \vec{P} - \hbar\vec{k}$$ ($\hbar\vec{k}$ transferred from wall to s.f.)

Square:

$$P'^2 = P^2 - 2\hbar\vec{P}\cdot\vec{k} + \hbar^2k^2$$

$$\underbrace{P'^2 - P^2}_{\overset{\shortparallel}{2M(E'-E)}} = \hbar^2k^2 - 2\hbar\vec{P}\cdot\vec{k}$$

$$2M(E'-E) = -2M\mathcal{E}$$ (energy transferred to s.f.)

or $$\mathcal{E} = \frac{\hbar\vec{P}\cdot\vec{k}}{M} - \frac{\hbar^2k^2}{2M}.$$

$$\vec{P}/M = \vec{v}, \text{ so}$$

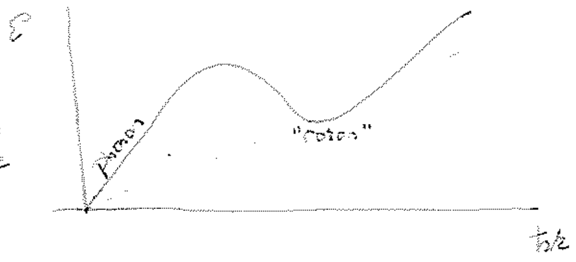
$$\mathcal{E} = \hbar k v\cos\theta - \underbrace{\frac{\hbar^2k^2}{2M}}_{\to 0 \text{ for wall mass large}}$$

$$v = \frac{\mathcal{E}}{\hbar k}\left[\cos\theta\right]^{-1}$$

Since $|\cos\theta| \leq 1$,

$$|v| \geq \frac{\mathcal{E}}{\hbar k} .$$

Now we have to look at excitations in the superfluid. The fluid is interacting, so excitations don't consist of moving isolated atoms, as in ideal gas, but are more like sound (as in air, water, solids). The dispersion curve looks like



longitudinal only, since no shear modulus in a liquid

For any k, the quantity $\frac{\mathcal{E}}{\hbar k}$ is the slope of a line going from the origin to $\mathcal{E}(k)$. The smallest such slope is — — — —

USE RULER

If v of flow $< \frac{\mathcal{E}_{roton}}{\hbar k_{roton}}$, the collision cannot occur.

New B-E condensate, e.g. Rb, NOT superfluid. [illegible]

Outline of course so far

Microcanonical Ensemble – ensemble of isolated systems

internal energy U, volume V, $\# N$ fixed

all microstates with U, V, N equally likely : number of such $= g(U,V,N)$

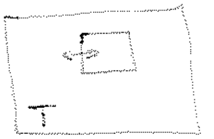
entropy $\sigma = k_B \ln g$

split into two subsystems that can exchange energy

most likely partition of energy equalizes temperature :

$$T = \left(\frac{\partial U}{\partial \sigma}\right)_{V,N}$$

Canonical Ensemble – ensemble of systems in thermal equilibrium w/reservoir



System in (many-body) state s with energy E_s
with probability

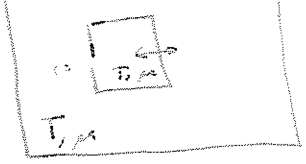
$$\frac{e^{-\beta E_s}}{Z}$$

where $Z = \sum_s e^{-\beta E_s}$

Helmholtz free energy $F = U - T\sigma = -k_B T \ln Z$
F minimized at equilibrium for fixed T, V, and N.

Grand-Canonical Ensemble – ensemble of system in thermal & diffusive equilibrium w/reservoir

System in (many-body) state $\underset{s}{N,}$ with energy $E_{s,N}$



w/ prob.
$$\frac{\lambda^N e^{-\beta E_{s,N}}}{\mathcal{Z}}$$

fugacity $\lambda = e^{\mu\beta}$

grand partition fnc. $\mathcal{Z} = \sum_{N,s} \lambda^N e^{-\beta E_{s,N}}$; chem. pot. $\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$

2/28/03

review :
1. ensembles
2. gases
3. laws

After spring break, we'll see that the Gibbs free energy, $G(T,P,N) = U - TS + PV$, is minimized at equilibrium for fixed T, P, and N.

Ideal (= non-interacting) gas

single-particle states ε_α

total energy is sum of occupied single-particle energies (= non-interacting)

Classical: $n \ll n_Q = \left(\frac{m k_B T}{2\pi\hbar^2}\right)^{3/2}$

equation of state $PV = N k_B T$

energy (equipartition) $U(T) = \frac{1}{2} \cdot \#\text{ degrees of freedom} \cdot k_B T = \frac{3}{2} N k_B T$ if monatomic

entropy (Sackur-Tetrode) $S = N\left[\ln(n_Q/n) + 5/2\right] + S_{\text{internal}}$

note: S contains $\hbar$ in it : if we take $\hbar \to 0$, $S \to \infty$

heat capacity $C_V = T\left(\frac{\partial S}{\partial T}\right)_{V,N} = \left(\frac{\partial U}{\partial T}\right)_{V,N} = \frac{3}{2} N k_B + C_V^{\text{internal}}$

"occupation" of a single-particle state $f_{MB}(T,\varepsilon) = e^{-\beta\varepsilon}$ OK if $\ll 1$

Example of using Sackur-Tetrode for monatomic ideal gas —

In adiabatic (isentropic) expansion at fixed N, show that $T \sim V^{-2/3}$.

$$S = N\left[\ln(n_Q/n) + 5/2\right] = \text{const.}$$

so $\frac{n_Q}{n} = \text{const.}$

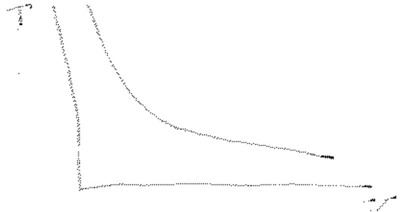
but $n_Q \sim T^{3/2}$, $n = \frac{N}{V} \sim V^{-1}$

so $T^{3/2} V = \text{const.}$

or

$$\boxed{T \sim V^{-2/3}}$$

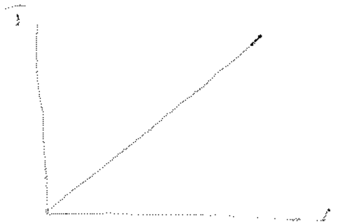
Sketch:



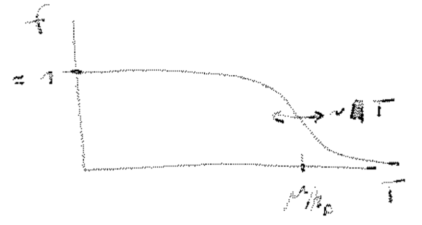
contrast to isobaric expansion:

$PV = N k_B T$,

so $T \sim V$

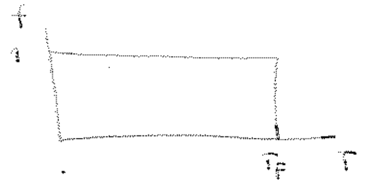


Fermi : occupation $f_{FD}(T,\mathcal{E}) = \frac{0 + e^{-(\mathcal{E}-\mu)\beta}}{1 + e^{-(\mathcal{E}-\mu)\beta}} = \frac{1}{e^{(\mathcal{E}-\mu)\beta}+1}$



$0 < T \ll T_F$: $\mu(T) = \mathcal{E}_F - \mathcal{O}(T^2/T_F)$

Zero temp. :



concentration (number density) $n = \int_0^{\mathcal{E}_F} d\mathcal{E}\, g(\mathcal{E})\, f(\mathcal{E})$ DOS $g(\mathcal{E}) \sim \begin{cases} \mathcal{E}^{-1/2} & 1D \\ \text{const.} & 2D \\ \mathcal{E}^{1/2} & 3D \end{cases}$

$C_V \sim \begin{cases} T & \text{for } T \ll T_F \text{ from graphical argument} \\ \text{const.} & \text{for } T \gg T_F \text{ equipartition} \end{cases}$

Bose

1) particle # not conserved

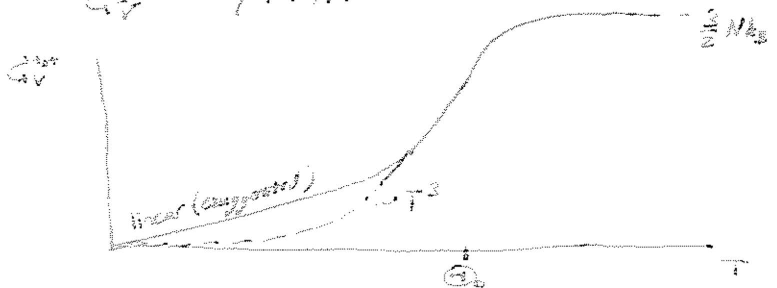
Planck : $f_{BE}(\hbar\omega) = \frac{1}{e^{(\hbar\omega-\mu)\beta}-1}$

Assertion: $\mu = 0$. Check: at $T=0$, $\beta=\infty$, so $f_{BE}(\hbar\omega) = 0$
$\Rightarrow$ no photons at $T=0$ in equilibrium.

$\frac{U}{V} = \int d\omega\, g(\hbar\omega)\, \hbar\omega\, f_{BE}(\hbar\omega) \sim T^4$

$C_V \sim T^3$ photons or phonons

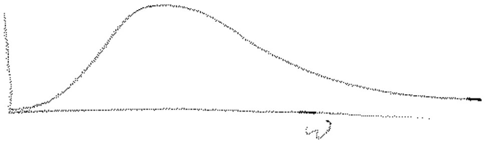
For metals, combine phonon (Bose) & e⁻ (Fermi) heat capacities:
$C_V^{\text{total}} = \gamma T + A T^3$



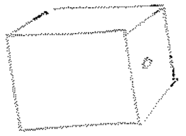
For $T \gg T_F$, it would asymptote to $3Nk_B$

per unit freq.: $\frac{U}{V} = \int d\omega \, u_\omega$

with u_ω



black-body radiation



flux ~ T^4 (Stefan-Boltzmann)

emissivity = absorbtivity = 1 − reflectivity

2) particle # conserved

$$f_{BE}(\epsilon) = \frac{1}{e^{(\epsilon-\mu)\beta} - 1}, \quad \mu(T) \le 0, \quad \text{fixed through}$$

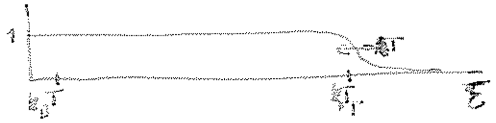
$$N = \int_0^\infty d\epsilon \, g(\epsilon) f_{BE}(\epsilon)$$

helium - just covered

---

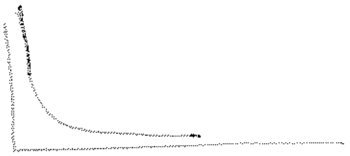
comparison of degenerate Bose & Fermi gases

Fermi



much higher energies than one would expect ($T_F \sim 10^4 - 10^5$ in metal)

Bose



lowest energy much more important than one would expect (e.g., $\frac{1}{k_B} \epsilon_{1^{st}\,exc.} \ll T \ll T_E$ gives almost all particles in ground state)

$\boxed{\text{Laws}}$

0. If A in equilib. w/ B, B ~ w/ C, A is in eq. with C.

$dU = \text{đ}Q + \text{đ}W, \; \text{đ}W = -PdV + \mu dN$

1. $dU = TdS - PdV + \mu dN$ (heat is work and work is heat)

$\text{đ}Q \le TdS$

2. $dS \ge 0$ (heat cannot of itself ... [illegible])
3. $S \to 0$ as $T \to 0$ (almost always)

alt.:
1) It's a zero-sum game.
2) You can't win.
3) You can break even only at $T=0$.

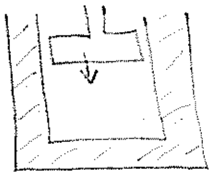
[Guest lectures 2003]

today: heat engine
Wed.: heat pump, refrig., etc.

3/3/2004 — return tests

Recall two ways (not only ways) of reversibly adding energy to a gas:

1)



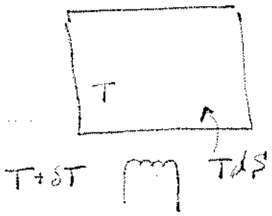
Adiabatic compression

$dU = -F\,dx = -P\,dV$ F = force, dx = displacement

mechanical $\boxed{\text{work}}$ done on gas

no change in entropy of system

2)



Isochoric $\boxed{\text{heat}}$ing

$dU = T\,dS$

no mechanical work
entropy increases

reversible only if
T difference infinitesimal
(idealization)

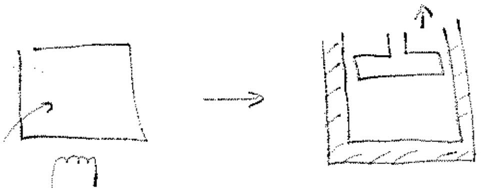
Discuss subtlety of reversible heating: put small box in a larger
box undergoing infinitely slow adiabatic compression.

In general, $dU = T\,dS - P\,dV$

$\equiv đQ + đW$

$đ$ as reminder: no separate entity in gas called "total heat Q" or "total work W"

example:



let adiabatic expansion do work (e.g., lift car)

We've converted some heat to work, so there's clearly no separate store of "heat" or "work"

Conversion not arbitrary, however, because there IS a separate store of entropy, S, in the system, and S can't be destroyed.

Engine: convert heat → work

In example above we could do a little, but eventually, as piston keeps going up, we run out of cylinder. Put another way, entropy keeps accumulating — need to dump it before we can continue.

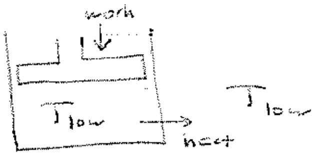
Cyclic engine: moves heat and work around, periodically returning to initial internal state.

example:

Carnot engine in 4 states (review) (ideal gas)

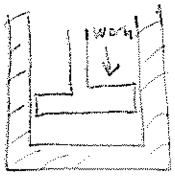
START ① $T = T_{low}$, max. V_1

A: compress isothermally
(i.e., in contact w/ reservoir T_{low})

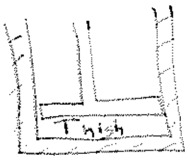


② $T = T_{low}$, $V_2 < V_1$

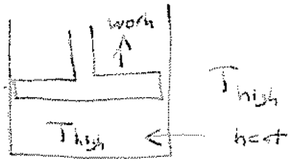
B: compress adiabatically
—gets hotter



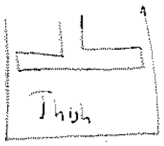
③ now it's at T_{high}, min. vol. V_3



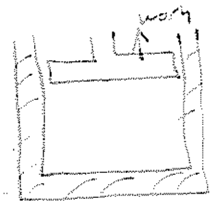
C: expand to V_4 in contact w/ reservoir T_{high} (isothermally)



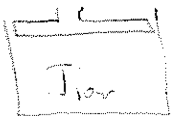
④ still at T_{high}, volume V_4



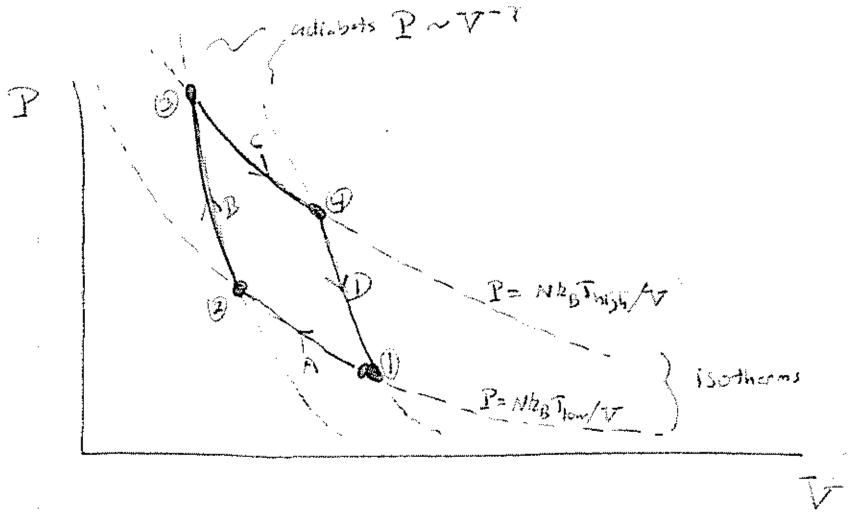
D: continue expansion adiabatically
—cools to T_{low}



① back to original



(88.3)

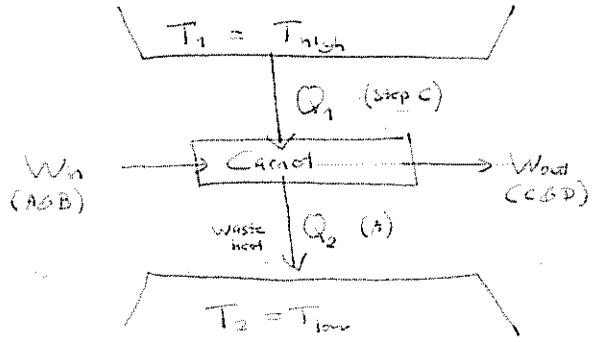


More work extracted in steps C & D than put back in steps A & B

(areas under curves — show)

more heat extracted from T_{high} in step C than dumped at T_{low} in step A.

Diagram for net effect of ONE CYCLE:



First law: $W_{in} + Q_1 = W_{out} + Q_2$

We'd like it if Q_2 were as small as possible, since it comes @ expense of useful work W_{out}.

Unfortunately, we cannot make it zero.

Second Law: total change in entropy of whole universe ≥ 0

Now $\Delta S_{system} = 0$ in one cycle

$$\Delta S_{Universe} = \underset{\substack{\text{hot} \\ \text{(step C)}}}{\Delta S_1} + \underset{\substack{\text{cold} \\ \text{(step A)}}}{\Delta S_2}$$

since work carries no entropy

$T_1 \Delta S_1 = -Q_1$; $T_2 \Delta S_2 = +Q_2$

so

$$\Delta S_{\text{Universe}} = -\frac{Q_1}{T_1} + \frac{Q_2}{T_2} \geq 0$$

$$\boxed{Q_2 \geq Q_1 \frac{T_2}{T_1}}$$ we cannot make it any smaller

Express in terms of net work $\Delta W = W_{out} - W_{in} = Q_1 - Q_2$.

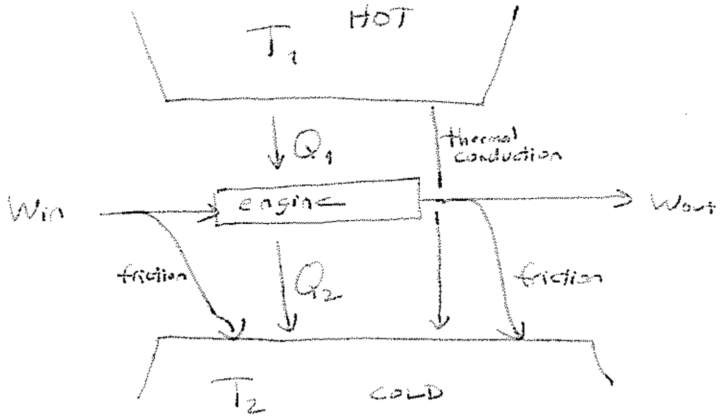
$$\Delta W \leq Q_1 - Q_1 \frac{T_2}{T_1}$$

efficiency $$\boxed{\eta \equiv \frac{\Delta W}{Q_1} \leq 1 - \frac{T_2}{T_1} = \frac{T_1 - T_2}{T_1}}$$

comments: ① If $T_1 = T_2$, net work $= 0$: we can't operate an engine at a single temperature

② If we could make $T_2 = 0$, we could have $Q_2 = 0$, i.e., all heat converted to work. So a zero-temperature reservoir would be very valuable.

③ What of inequalities? Irreversible processes (e.g., friction, sudden expansion) convert work → heat uselessly:



friction, conduction add to Q_2 at the expense of W_{out}

88.5

3/5/2004

Carnot cycle for ideal gas – redraw PV from p. 88.3

Step	process	work on gas	heat added to gas
A	isothermal compression	$-\int_{V_1}^{V_2} P\,dV = -\int_{V_1}^{V_2} Nk_B(T/V)\,dV$ $= +Nk_B T_\ell \ln V_1/V_2$	$-Nk_B T_\ell \ln V_1/V_2$ since internal energy unchanged
B	adiabatic comp.	$\frac{3}{2}Nk_B(T_h - T_\ell)$	—
C	isothermal expansion	$-Nk_B T_h \ln V_4/V_3$	$Nk_B T_h \ln V_4/V_3$
D	adiabatic exp.	$\frac{3}{2}Nk_B(T_\ell - T_h)$	—

Check: 1st law ✓

$$W_{out} - W_{in} = Nk_B\left[-T_\ell \ln V_1/V_2 - \frac{3}{2}(T_h - T_\ell) + T_h \ln V_4/V_3 + \frac{3}{2}(T_h - T_\ell)\right]$$

$$= Nk_B\left[T_h \ln V_4/V_3 - T_\ell \ln V_1/V_2\right]$$

too many diff. volumes, so try to eliminate some

(monatomic) Since $P \sim V^{-5/3}$ on an adiabat (say B),

$$\underbrace{P_2}_{Nk_BT_\ell/V_2} V_2^{+5/3} = \underbrace{P_3}_{Nk_BT_h/V_3} V_3^{+5/3}$$

$$\left.\begin{aligned} \text{so} \quad T_\ell V_2^{2/3} &= T_h V_3^{2/3} \\ \text{Similarly,} \quad T_h V_4^{2/3} &= T_\ell V_1^{2/3} \end{aligned}\right\} V_4 V_1^{-1} V_2 = V_3$$

[subst. $T_\ell = T_h V_4^{2/3} V_1^{-2/3}$, then cube]

$$\downarrow$$

$$\frac{V_4}{V_3} = \frac{V_1}{V_2}$$

Short-cut: every step reversible, so $\Delta S_1 + \Delta S_2 = 0$

$\frac{Q_h}{T_\ell} + \frac{Q_c}{T_h} = 0$, so (see above)

$\frac{V_4}{V_3} = \frac{V_1}{V_2}$

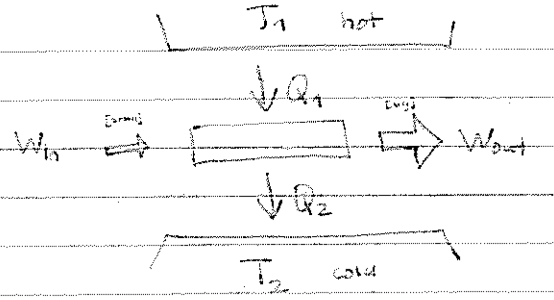
$$\text{Thus} \quad W_{out} - W_{in} = Nk_B(T_h - T_\ell)\ln(V_4/V_3)$$

heat drawn from hot reservoir (step C) $= Nk_B T_h \ln(V_4/V_3)$

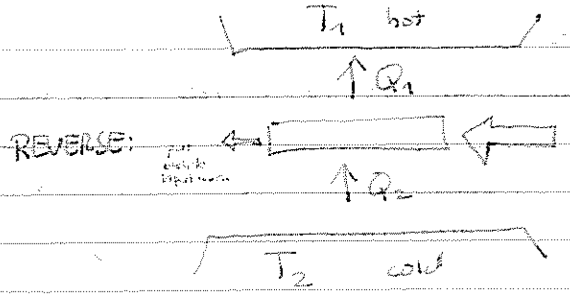
$$\text{efficiency} \quad \eta = \frac{W_{out} - W_{in}}{Q_{hot}} = \frac{T_h - T_\ell}{T_h}$$ ✓ agrees w/ 2nd law

(38.6)

ENGINE:



refrigerator / air conditioner / heat pump



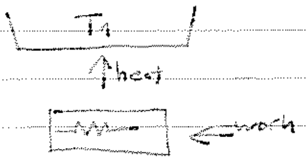
each cycle: pay TECO
move heat from cold reservoir
to hot reservoir (but not "of itself")

terminology:

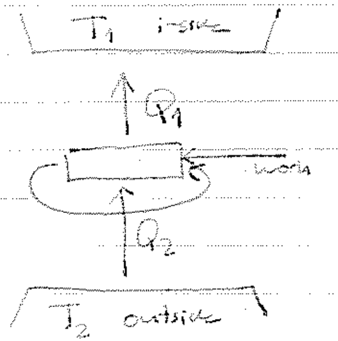
	T_1 hot	T_2 cold
"refrigerator"	room	food
"air conditioner"	outside	inside
"heat pump"	inside	outside

all same device - different figures of merit : see book

perfect heat pump more efficient than resistive heating:

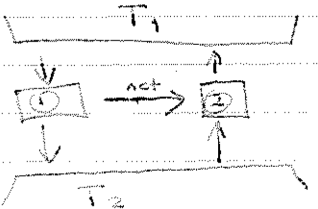


looks great: 100% of work → heat.
How can one possibly do better?



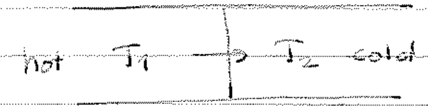
problem 8.1

We previously derived the Carnot efficiency $\frac{\Delta W}{\Delta Q_{hot}} = \frac{T_1 - T_2}{T_1}$ from just 1st & 2nd laws, and we verified the result for the ideal gas. We can equivalently argue that any two reversible engines must have same efficiency.



If engine 2 were more efficient than engine 1, we could extract work w/o any change in reservoirs (& vice versa).

Irreversible heat transfer by thermal conduction



Heat xfer $\bar{d}Q = -T_1 dS_1 = T_2 dS_2$

entropy change on left $= dS_1 = -\frac{\bar{d}Q}{T_1}$

on right $dS_2 = +\frac{\bar{d}Q}{T_2}$

net entropy change $dS = \bar{d}Q\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \frac{T_1 - T_2}{T_1 T_2}\,\bar{d}Q$

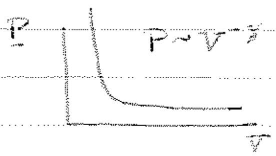
For $T_1 > T_2$, $\bar{d}Q > 0$, so $dS > 0$

For $T_1 < T_2$, $\bar{d}Q < 0$, so $dS > 0$ still

Only in limit that T_1 & T_2 differ infinitesimally, can heat be transferred reversibly (purely theoretical device)

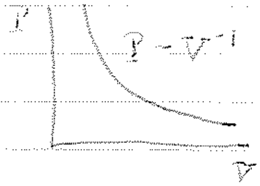
[illegible]

Connect processes to natural energies



1. Adiabatic: $dU|_S = -PdV = \bar{d}W$

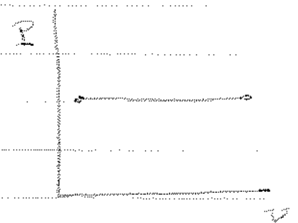
total work performed = increase in INTERNAL energy



2. isothermal $dU|_T = TdS - PdV = TdS + \bar{d}W$

$$\bar{d}W|_T = dU - TdS = dU - d(TS) \quad \text{since } dT = 0$$
$$= d(U - TS)$$
$$= dF|_T$$

total work performed = increase in HELMHOLTZ FREE energy



3. isobaric $\bar{d}Q|_P = TdS = dU + PdV$

$$= dU + d(PV) \quad \text{since } dP = 0$$
$$\equiv dH|_P$$

heat added = increase in ENTHALPY

where $H = U + PV$ "enthalpy"

[illegible]

another way to think of it :

Other kinds of work:

$\bar{d}W = -PdV + \mu dN +$ electrical $+ \ldots$

not really interested in $-P\,dV$, since as $V \uparrow$ or $\downarrow$, we neither recover work nor pay for it – atmosphere supplies everything.

Thus define "effective work" $\bar{d}W' = \bar{d}W + P\,dV$ (subtracts $-P\,dV$)

$$= \bar{d}W + d(PV) \quad \text{since } dP = 0$$
$$= dU + d(PV) - \bar{d}Q$$
$$= dH - \bar{d}Q \quad \text{(all at const. pressure)}$$

Define Gibbs free energy

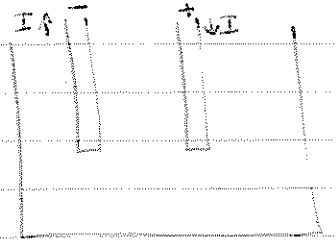
$$G = F + PV = U - TS + PV = H - TS$$

Constant P AND T:

$$dG\big|_{T,P} = dH - T\,dS = dH - \bar{d}Q = \bar{d}W'\big|_{T,P}$$

skip 2007

example from book: electrolysis



const. P & T

in soln: $H_2SO_4 \rightleftarrows 2H^+ + SO_4^{--}$

negative electrode: $2H^+ + 2e^- \rightarrow H_2$ (bubbles)

positive: $SO_4^{--} + H_2O \rightarrow H_2SO_4 + 2e^- + O$

$2O \rightarrow O_2$ (bubbles)

net: $2H_2O \rightarrow 2H_2 + O_2$ with transfer of two electrons $- \rightarrow +$

effective work (subtracts vol. change) to dissociate one mole of water:

$$W' = \Delta G = -G(H_2O) + G(H_2) + \tfrac{1}{2}G(O_2) = +237\text{ kJ}$$

= power · time

= current · voltage · time

= voltage · charge

charge to dissociate one mole $= 2N_A \cdot (-e) = -1.93 \cdot 10^5$ Coul

$\Rightarrow$ voltage $= 1.229$ V

any more: extra power → heat (useless)

any less: don't break down water

reverse process: fuel cell

3/17/03 today: review, various thermodynamic potentials

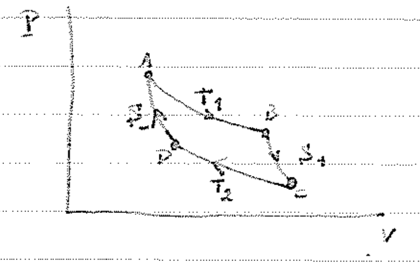
Wed.: Chemistry

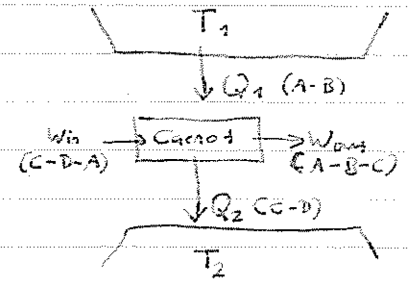
skip 3/15/04

Offer to answer questions on test, homework

Prob. [illegible]: fixed power of temp (e.g., for Fermi, $C_V \sim T$ if $T \ll T_F$)

review of Ch. 8





Net mechanical work done in cycle = $W_{out} - W_{in}$

= net heat flow through engine $= Q_1 - Q_2$

= area enclosed

For any reversible cyclic process, $\dfrac{\Delta W}{\Delta Q} = \dfrac{T_1 - T_2}{T_1}$

- doesn't depend on ideal gas, path, only on reversibility

start here 3/15/04

work $\text{đ}W = dU - \text{đ}Q$, $\text{đ}Q = T\,dS$, so $\text{đ}W = dF$ (reversible) [illegible]

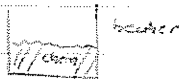
TD defn of entropy: $dS = \frac{1}{T}\text{đ}Q$; of temperature: $T_2/T_1 = Q_2/Q_1$ on isotherms

I believe Dr. Witanachchi got as far as "effective work" and the example with the fuel cell.

Effective work $\text{đ}W' = \text{đ}W - $ (mechanical work)

$= \text{đ}W + P\,dV$

(rationale:



open to atmosphere - neither recover nor pay for work assoc. with volume change)

If $dP = dT = 0$,

$\text{đ}W' = dF + P\,dV \equiv dG$

define Gibbs free energy $G = F + PV = U - TS + PV$

[mention historical session at Austin APS mtg.]

internal energy dU = heat + work (done on system)

Some types of work:

mechanical $-P\,dV$

chemical $\mu\,dN$ (for ea. species, i.e., $\mu_1\,dN_1 + \mu_2\,dN_2 + \ldots$)

magnetic:

energy stored in field $U_m = \frac{1}{8\pi}\int_V B^2\,dV$ (s.t. w/ μ_0 in it in MKS units)

$$B = H + 4\pi M$$

derivation involved, not in KBK, so I'll just quote results:

$$dU \rightarrow dU + H\,d(MV)$$ all assuming uniform M

$$dF \rightarrow dF + H\,d(MV)$$

$$dG \rightarrow dG - MV\,dH$$

Start here 2009

Leave off magnetic work.

$$U = U(S, N, V)$$

U assumed to be determined completely by S, N, V ("microcanonical ensemble")

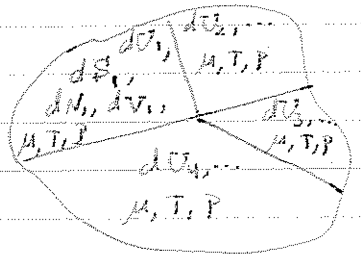
$$dU = \underbrace{\left(\frac{\partial U}{\partial S}\right)_{N,V}}_{T} dS + \underbrace{\left(\frac{\partial U}{\partial N}\right)_{S,V}}_{\mu} dN + \underbrace{\left(\frac{\partial U}{\partial V}\right)_{S,N}}_{-P} dV$$

① $dU = T\,dS + \mu\,dN - P\,dV$

U, S, N, V extensive

μ, T, P intensive and uniform in equilibrium

Add up many little pieces:



② $U = TS + \mu N - PV$

We don't always have knobs for S, N, V. If instead, we control N, T, P, it's convenient to define

Gibbs ③ $\quad G \equiv U - TS + PV$

$\quad = \mu N$ by ②, so μ is Gibbs free energy per particle

$$dG = dU - TdS - SdT + PdV + VdP$$

④ $\quad = \mu dN - SdT + VdP \quad$ by ① $\quad \Rightarrow G = G(N,T,P)$

If P, T, and N are constant (system at equilibrium), $dG = 0$.
More generally,

$$dG(N,T,P) = \underbrace{\left(\frac{\partial G}{\partial N}\right)_{T,P}}_{\mu} dN + \underbrace{\left(\frac{\partial G}{\partial T}\right)_{N,P}}_{-S} dT + \underbrace{\left(\frac{\partial G}{\partial P}\right)_{T,N}}_{V} dP$$

identifications by ④

If we control N, T, and V, define

Helmholtz $\quad F = U - TS$

$$dF = dU - TdS - SdT$$

$\quad = \mu dN - PdV - SdT \quad$ by ① $\quad \Rightarrow F = F(N,T,V)$

$$dF(N,T,V) = \underbrace{\left(\frac{\partial F}{\partial N}\right)_{T,V}}_{\mu} dN + \underbrace{\left(\frac{\partial F}{\partial T}\right)_{N,P}}_{-S} dT + \underbrace{\left(\frac{\partial F}{\partial V}\right)_{N,T}}_{-P} dV$$

If we control S, P, and N, define

Enthalpy $\quad H(S,P,N) = U + PV$

$$dH = dU + PdV + VdP \overset{①}{=} TdS + \mu dN + VdP \quad H=H(S,P,N)$$

$$= \underbrace{\left(\frac{\partial H}{\partial S}\right)_{P,N}} dS + \underbrace{\left(\frac{\partial H}{\partial P}\right)_{S,N}}_{V} dP + \underbrace{\left(\frac{\partial H}{\partial N}\right)_{S,P}}_{\mu} dN$$

It can be shown that

$$C_P = \left(\frac{\partial H}{\partial T}\right)_{N,P}$$

3/19/03 Monday: review, formalism
today: chemistry
Friday: chemistry, maybe superfluid fountain effect
CORRECTION ON HW10

$$F(T,V,N) = U - TS \quad ; \quad dF = -S\,dT - P\,dV + \mu\,dN$$
$$G(T,P,N) = U - TS + PV \quad ; \quad dG = -S\,dT + V\,dP + \mu\,dN$$

We found $\left(\frac{\partial G}{\partial N}\right)_{T,P} = \mu$ and $G = \mu N$.

However, although $\left(\frac{\partial F}{\partial N}\right)_{T,V} = \mu$, $F \neq \mu N$.

explanation/illustration for classical monatomic ideal gas

$\mu = k_B T \ln(n/n_Q)$. Since $n = \frac{N}{V}$, and $n_Q \sim T^{3/2}$,

$\mu = \mu(N,T,V)$. These are the variables of F.

If we hold T, V constant, μ is not ind. of N.
So we can't ~~integrate~~ just multiply by N to get F. It is still intensive, since $\mu = $ const.
if N & V scale together. However, this doesn't help us get $F = \int_0^N dN' \mu(N',T,V)$

Contrast when μ put in terms of the variables proper to G:

$$\mu = k_B T \ln\left(\frac{N}{V n_Q}\right) = k_B T \ln\left(\frac{P}{k_B T n_Q}\right) = \mu(T,P) \quad \text{no } N \text{ left}$$

Thus we can integrate:

$$\left(\frac{\partial G}{\partial N}\right)_{T,P} = \mu(T,P)$$

apply $\int_0^N dN'$ to both sides

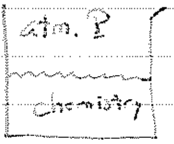
$$G(N,T,P) = \mu(T,P)\int_0^N dN' = N\mu$$

3/21/03

Chemistry

$$A + B \rightleftharpoons AB \qquad (\text{"aye-bee ide"})$$

Since the reaction can go either way, in equilibrium $(T>0)$ there may be some amount of each of the three species, A, B, and AB.



$$dT = dP = 0$$

so it's the Gibbs free energy we're after.

$$0 = dG(T, P, N_A, N_B, N_{AB}) = -S\,dT + V\,dP + \mu_A dN_A + \mu_B dN_B + \mu_{AB} dN_{AB}$$

Since $dT = dP = 0$,

$$\mu_A dN_A + \mu_B dN_B + \mu_{AB} dN_{AB} = 0$$

also $dN_A = dN_B = -dN_{AB}$ (conservation of atoms)

so $(\mu_A + \mu_B - \mu_{AB})\, dN_A = 0$

$$\boxed{\mu_A + \mu_B - \mu_{AB} = 0}$$

More generally, we might have other integer coefs, e.g.,

$$A + B + 2C \rightleftharpoons BC + AC$$

or $\nu_1 A_1 + \nu_2 A_2 + \dots + \nu_l A_l = 0$

i	species	ν_i
1	A	1
2	B	1
3	C	2
4	BC	-1
5	AC	-1

generalization of box: $\boxed{\sum_j \nu_j \mu_j = 0}$

3/5/04

4/27/07

If each constituent is (effectively) an ideal gas, we can use the form for μ derived at the same time as Sackur-Tetrode:

$$\mu_j = k_B T \left[\ln\left(\frac{n_j}{n_j^Q}\right) - \ln Z_j^{int} \right]$$ where n_j is conc. of species j, Z_j^{int} the internal partition fn

$$= k_B T \left[\ln n_j - \ln\left(n_j^Q Z_j^{int}\right) \right]$$

$$0 = \sum_j \nu_j \mu_j = k_B T \sum_j \left[\nu_j \ln n_j - \nu_j \ln\left(n_j^Q Z_j^{int}\right) \right]$$

$$\sum_j \ln\left(n_j^{\nu_j}\right) = \sum_j \ln\left(\left(n_j^Q Z_j^{int}\right)^{\nu_j}\right)$$

$$\ln \prod_j n_j^{\nu_j} = \ln \prod_j \left(n_j^Q Z_j^{int}\right)^{\nu_j}$$

$$\boxed{\prod_j n_j^{\nu_j} \equiv K(T)}$$ "law of mass action"

where $K(T) = \prod_j \left(n_j^Q Z_j^{int}\right)^{\nu_j}$ depends on reaction & T, not on concentration

$$= \prod_j n_j^{Q\,\nu_j} \exp\left[-\nu_j F_j^{int} \beta\right]$$ w/ $F_j^{int} = -k_B T \ln Z_j^{int}$

ignore others spin (nuclear spin)

Example: $H_2 \rightleftharpoons 2H$

write $n_{H_2} = [H_2]$, $\nu_{H_2} = 1$

$n_H = [H]$, $\nu_H = -2$

mass action $\Rightarrow \dfrac{[H_2]}{[H]^2} = K(T)$

K also absorbs this into the other

$$\log K(T) = \ln n_{H_2}^Q - 2\ln n_H^Q - F_{H_2}^{int}\beta + 2F_H^{e\,spin}\beta$$

Binding energy is in $F_{H_2}^{int}$: tight binding → F negative → K large → relative $[H_2]$ ↑

but not infinite: why isn't it H_2 in space?

$[H]^2$ in denominator represents density for two atomic hydrogens to meet – very rare. Thus even if K is big, $[H_2]$ can be quite small, since $\frac{1}{[H]^2}$ is big. Most of the hydrogen in space is atomic.

3/30/04

Extreme: $T=0 \rightarrow \beta=\infty \rightarrow$ only energy (not entropy) matters
$K \rightarrow +\infty$
so all goes to H_2 in equilibrium

Whether this will actually happen as universe expands and cools would require a detailed calc.: although in equilibrium at $T=0$, everything is H_2, it may take forever to reach that equilibrium since the atomic H will be so far apart.

(Need "dark energy" → proton decay)
at 60T

Similar:

$H_2O \rightleftharpoons H^+ + OH^-$

example problem 9.5: $A + \bar{A} \rightleftharpoons$ energy

$$[A][\bar{A}] = n^2 \text{ since they're equal}$$
$$= K = n_Q^2 e^{-2\beta F}, \quad F = \tfrac{1}{2}\Delta \quad \text{(explain)}$$
$$= n_Q^2 e^{-\beta\Delta}.$$

given: $\beta\Delta = 20$.

Mc^2 & Δ differ because K&K are thinking of particle-hole, not particle-antiparticle. Warning: M_A need not equal $M_{\bar{A}}$, but in a nearly-free-electron semiconductor it might be close. $[A] = [\bar{A}]$ means undoped (neither n-type nor p-type).

$$n_Q = \left(\frac{M k_B T}{2\pi\hbar^2}\right)^{3/2} \approx 1.25\cdot 10^{19}\,\text{cm}^{-3}, \text{ so } n = n_Q e^{-\beta\Delta/2} = 5.7\cdot 10^{14}\,\text{cm}^{-3}$$

(c): spin: $\lambda = \frac{n}{n_Q} \rightarrow \frac{n}{n_Q Z^{int}}$, $Z^{int} \rightarrow 2$, so $n_Q \rightarrow 2n_Q$
get $n \rightarrow 2n = 1.14\cdot 10^{15}\,\text{cm}^{-3}$

3/21/03 Wed.: law of mass action
today: finish —
thermodynamics of superfluidity
start phase transitions
Mon.: phase transitions

$$\prod_j n_j^{\nu_j} = K(T) = \prod_j (n_j^{Q})^{\nu_j} \exp[-\nu_j F_j^{int}\beta]$$

[make sure I didn't accidentally call K a "rate"]

Alternative derivation of law of mass action (from book)

$$A + B \rightleftarrows AB$$

C = rate of forward reaction
D = rate of reverse.

ideal gas assumption →

$$\frac{dn_{AB}}{dt} = C n_A n_B - D n_{AB}$$

units of C: $\frac{cm^3}{sec}$
of D: $\frac{1}{sec}$

C & D may depend on T but not on concentration

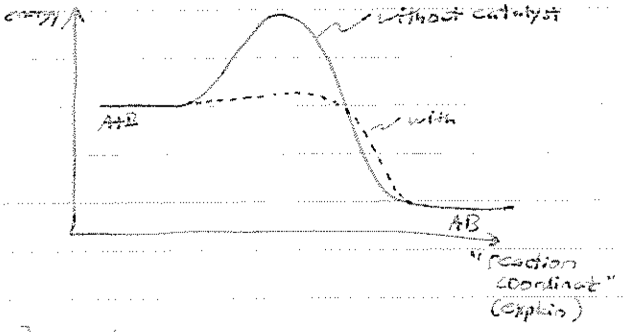
At equilibrium $\frac{dn_{AB}}{dt} = 0$, so

$$C n_A n_B = D n_{AB}$$ "principle of detailed balance" forward = reverse

or $$\frac{n_A n_B}{n_{AB}} = D/C = K$$ law of mass action

Law of mass action contains less information than the rate constants C, D above — C & D give not only equilibrium concentrations (as does K) but also rates at which reactions proceed. K&K suggest a catalytic process with catalyst E:

$$A + E \rightleftarrows AE$$
$$AE + B \rightleftarrows AB + E$$



So long as these reactions proceed fast enough that $n_{AE} \ll n_A, n_B, n_{AB}$, the equilibrium ratios must be the same as for the uncatalyzed reaction: K = [above] makes no reference to rates (like C, D) or pathway, only to energy and entropy differences.

example 9.4:

a) By induction.

For $N=1$, we have by the law of mass action

$$\frac{[1][1]}{[2]} = K_1$$ in agreement with eq. 49.

Note book using convention opposite that on p 269 for forward vs. backward

Assume (49) for $N-1$, so that

$$[N] = [1]^N / (K_1 K_2 \cdots K_{N-1})$$

Then $$\frac{[N][1]}{[N+1]} = K_N$$

$$[N+1] = [1][N] / K_N \Rightarrow (49) \checkmark$$

b) $$K_N = \frac{n_Q(1)\, n_Q(N)}{n_Q(N+1)} \exp\left[\beta\left(F_{N+1} - F_N - F_1\right)\right]$$ directly from the law of mass action for $N+1 \rightleftarrows (N+1)$

c) $$\frac{[N+1]}{[N]} = [1]/K_N$$, Then plug in numbers

told to set $n_Q(N+1) \approx n_Q(N)$, $\Delta F = F_{N-1} - (F_N + F_1) = 0$

then $$K_N = n^Q(1) = \left(\frac{M k_B T}{2\pi\hbar^2}\right)^{3/2}$$
$$= 2.76 \cdot 10^{27}\,\mathrm{cm}^{-3}$$

$M = 200$ a.m.u. $= 200 \cdot 1.67 \cdot 10^{-24}$ g
$[1] = 10^{20}\,\mathrm{cm}^{-3}$
$T = 300\,\mathrm{K}$

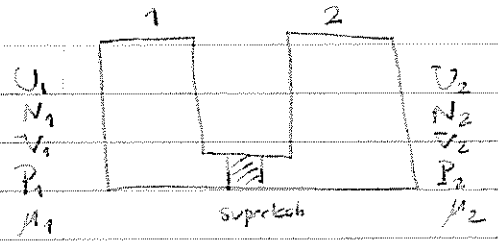
so $$\frac{[N+1]}{[N]} = [1]/K_N = 3.6 \cdot 10^{-8}$$ $\Rightarrow$ don't get large N

d) To get large N, we need

$$K_N \lesssim [1]$$
$$\|$$
$$n^Q(1) \exp[\beta \Delta F]$$

$$\Delta F \lesssim k_B T \ln\left(\frac{[1]}{n^Q(1)}\right) = -7.1 \cdot 10^{-13}\,\mathrm{erg} = -0.44\,\mathrm{eV}$$

(98)



Heat side 1, then turn off – recall $T_1 \neq T_2$, $P_1 \neq P_2$ (at bottom)

What are conditions of equilibrium? Total $U = U_1 + U_2$, $V = V_1 + V_2$ (assumes incompressibility), and $N = N_1 + N_2$ are conserved (after heater turned off). So ~~is total $S = S_1 + S_2$,~~ are S_1 and S_2 separately since only the condensate flows, and it carries no entropy. Thus $dU = 0$ in any process. In particular,

$$\left(\frac{\partial U}{\partial N_1}\right)_{S,V,N} = 0 = \left(\frac{\partial U_1}{\partial N_1}\right)_{S_1} + \left(\frac{\partial U_2}{\partial N_1}\right)_{S_2} = \left(\frac{\partial U_1}{\partial N_1}\right)_{S_1} - \left(\frac{\partial U_2}{\partial N_2}\right)_{S_2} = \mu_1 - \mu_2$$

So chemical potentials are equal at equilibrium as usual.

However, that's it. We cannot conclude that temps. are equal in equilibrium, because there's no thermal contact. Normally we would do so with

$$\left(\frac{\partial U}{\partial S_1}\right)_{S,V,N} = 0 = \ldots$$

However $dS_1 = 0$ in any process.

Now to calc P & T:

differential TD identity : $dU = TdS - PdV + \mu dN$ ①
integral " " : $U = TS - PV + \mu N$ ②

differential of ②:

$$dU = TdS + SdT - PdV - VdP + \mu dN + Nd\mu$$

Subtract ① to get another differential identity:

$$0 = SdT - VdP + Nd\mu \qquad ③$$

Since equilibrium requires $\mu_1 = \mu_2$ we have $d\mu_1 = d\mu_2 = 0$. So, for side $i = 1, 2$,

$$S_i\, dT_i - V_i\, dP_i = 0$$

$$\frac{dP_i}{dT_i} = \frac{S_i}{V_i} \sim \text{all in normal component}$$

If $dT_i = 0$, as for normal fluid, we'd have $dP_i = 0$, and all three of μ, T, P would equilibrate.

→ since $\frac{S}{V} > 0$

Fountain effect: if T on one side goes up, so does pressure. The only way for P↑ is for mass to flow, so it does.

Showed phase diagrams out of Desloge to dispell two myths: 1) there are only 3 phases of water; (2) there are as many as 3 phases of water

3/24/05

3/24/03 last week: chemical equilibrium
today: phase transitions
Clausius - Clapeyron
Wed.: van der Waals gas

What's meant by "phase" and "transition"?

Some phases of matter:

Solid: shear modulus $\neq 0$
- crystal: long-range translational order
  - periodic
  - quasiperiodic ("quasicrystal")
- amorphous, glass (may be only metastable)

Fluid: no LRO$^{\text{transl.}}$, shear modulus $= 0$
- ideal $^{\text{(Eulerian)}}$ liquid: incompressible $\left(-V\left(\frac{\partial P}{\partial V}\right)_{T \text{ or } S} = \infty\right)$
- ⋮
- ideal gas: $PV = Nk_BT$ $\quad \left(-V\left(\frac{\partial P}{\partial V}\right)_T = nk_BT,\ n = N/V\right)$

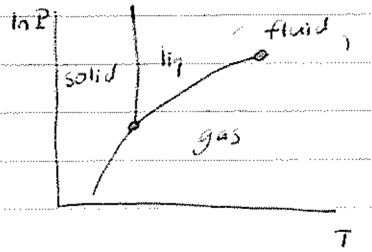
continuum ↓

Other phases: liquid crystals (nematic, smectic), 2dim'l phases (no LRO but still have transitions), superfluids, 2DEG, viscoelastics, ...

So what's changing across a phase transition?

Certainly in H_2O, density.

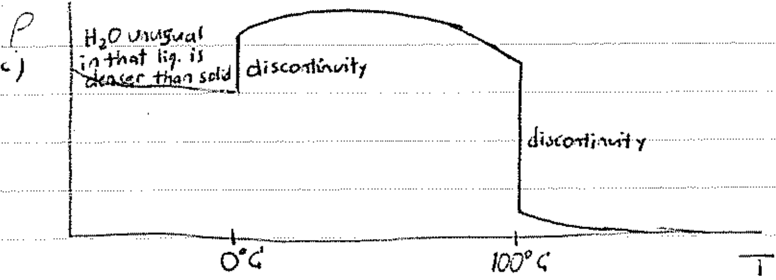
Put up Desloge



point out critical & triple points

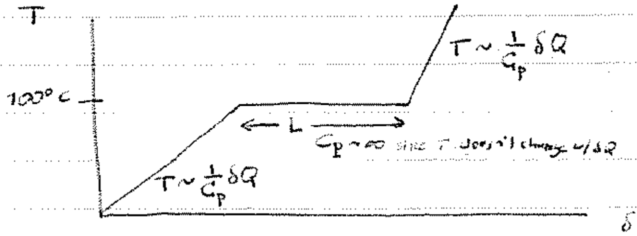
Fix $P = 1$ atm (say).

(schematic)



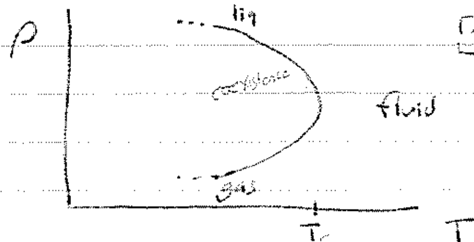
These transitions called "first order" because the 1st deriv. of free energy (with T or P) is discontinuous.

Latent heat: e.g., boiling at 1 atm



⇒ heat added (e.g., time over burner)

Right at critical pressure, $L = 0$, but C_p still diverges: "second-order" xition (2^{nd} deriv. of free energy is discontinuous).



PRESSURE is 3^{rd} axis

Peculiar behavior at crit pt.:

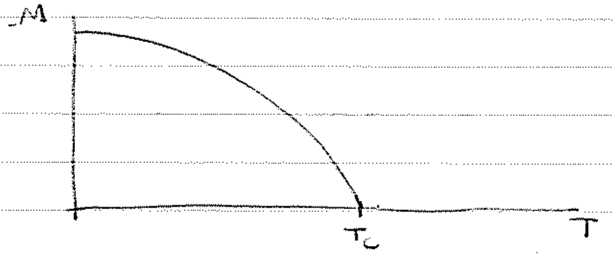
$$\lim_{T \to T_c^-} \rho_\ell - \rho_g = A(T_c - T)^\beta$$

A depends on system

$\beta = 0.325 \pm 0.0015$ (theory)

$0.316 - 0.327$ expts. for a large # of systems $\overset{I}{(}$don't know H_2O)

Magnetization of a ferromagnet (or staggered magn. of an antiferromagnet)



near T_c

$M \sim A(T_c - T)^\beta$ same β

$DyAlO_3$ $\beta = 0.311 \pm 0.005$ expt.

Calculating "universal" critical exponents such as β is the work of the modern theory of 2^{nd}-order phase transitions – maybe a couple of lectures toward end of course

---

Coexistence line in a 1^{st}-order phase xition (Clausius–Clapeyron)

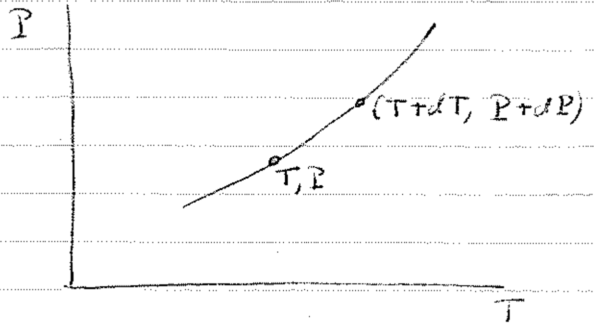
Call the two phases l, g (liq-gas but could be liq-solid or solid-gas)

Coexistence criteria:

$$T_l = T_g$$
$$P_l = P_g$$
$$\mu_l = \mu_g$$

Since we control T, P, not μ, externally, write

$$\mu = \mu(T,P) = \mu_l(T,P) = \mu_g(T,P)$$



To compute coexistence curve, consider two nearby points as shown; the goal is to find $P(T)$.

[illegible]/3/05

$$\begin{cases} \mu_\ell(T,P) = \mu_g(T,P) \\ \mu_\ell(T+dT,\ P+dP) = \mu_g(T+dT,\ P+dP) \end{cases}$$

Taylor expand second:

$$\cancel{\mu_\ell(T,P)} + dT\left(\frac{\partial \mu_\ell(T,P)}{\partial T}\right)_P + dP\left(\frac{\partial \mu_\ell(T,P)}{\partial P}\right)_T = \cancel{\mu_g} + dT\left(\frac{\partial \mu_g}{\partial T}\right)_P + dP\left(\frac{\partial \mu_g}{\partial P}\right)_T$$

N_ℓ, N_g Assume numbers constant as we move along coexistence line. [illegible]

Cancel equal quantities above.

To evaluate the partial derivatives:

$$\mu = G/N, \quad N \text{ const.}, \quad \text{so} \left(\frac{\partial \mu}{\partial T}\right)_P = \frac{1}{N}\left(\frac{\partial G}{\partial T}\right)_P = -\frac{S}{N} \equiv -s$$

minus entropy per particle

$$\& \left(\frac{\partial \mu}{\partial P}\right)_T = \frac{1}{N}\left(\frac{\partial G}{\partial P}\right)_T = \frac{V}{N} \equiv v$$

Inverse concentration, or volume per particle

so

$$-dT s_\ell + dP v_\ell = -dT s_g + dP v_g$$

$$dP(v_g - v_\ell) = dT(s_g - s_\ell)$$

$$\boxed{\left.\frac{dP}{dT}\right|_{\substack{\text{coex.}\\ \text{line}}} = \frac{s_g - s_\ell}{v_g - v_\ell} = \frac{\Delta s}{\Delta v}}$$

Δs = change in entropy as a molecule moves from gas to liq.

Δv = change in volume...

Latent heat = $T\Delta s$

[illegible] so $\boxed{\frac{dP}{dT} = \frac{L}{T\Delta v}}$ Clausius - Clapeyron

For the liq.-gas xition not too close to the crit point we may make two good approximations:

$$v_g \gg v_\ell, \text{ so } \Delta v \approx v_g \underset{\substack{\text{ideal}\\ \text{gas}}}{\approx} \frac{k_B T}{P}.$$ Then

$$\boxed{\frac{dP}{dT} = \frac{LP}{k_B T^2}}$$

. If additionally, L is approx. ind. of T along the coexistence curve, we can integrate:

$$\frac{dP}{P} = \frac{L}{k_B}\frac{dT}{T^2}$$

$$\ln P = -\frac{L}{k_B}\cdot\frac{1}{T} + \text{const.}$$

$$P(T) = P_0 \exp\left(-\frac{L}{k_B T}\right)$$

(L ind. of T along curve)

Latent heat:

move one over from gas to liq.: @ constant P

$$dU_g = T\,dS_g - P\,dV_g - \mu\,dN$$
$$dU_l = T\,dS_l - P\,dV_l + \mu\,dN$$

$$d(U_g+U_l) = \underbrace{T(dS_g+dS_l)}_{dL} - P(dV_g+dV_l)$$

Signs: $dS_g + dS_l$ is the total change in entropy when dN particles are moved from gas to liquid.

$$dL = d(H_g + H_l) \quad \text{(at constant } P\text{)} \qquad (H \equiv U + PV)$$

$$L = \Delta H$$

change in enthalpy

3/26/03 Mon.: phase transitions

today: mean-field theory

van-der-Waals eqn. of state

Fri.: Landau theory

binary mixtures

Ideal gas: $PV = Nk_BT$ no phase transition (except maybe to black hole at $T=0$), so we need to replace

van der Waals: $P \rightarrow P + \text{something}$

$V \rightarrow V - \text{something}$

Detailed interactions are averaged – example of a mean-field theory.

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Simplest MFT is Curie-Weiss theory of ferromagnetism, so start there.

First, recall paramagnet (Ch. 3):

$$\mathcal{H} = -B^{ext} \sum_i' s_i$$

Easy: every spin has exactly the same environment.

We found magnetization $\mathcal{M} = \langle 2\sigma \rangle \mu / V = n\mu \tanh\left(\frac{\mu B}{k_B T}\right)$

$\langle 2\sigma \rangle$ = spin excess = $\langle N_\uparrow - N_\downarrow \rangle = N\langle s \rangle$

[μ = moment per spin

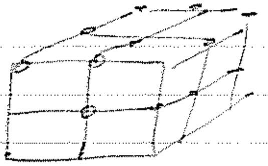
$n = N/V$

Model of a FM: no external field

hard for the same reason Chess, Go are hard

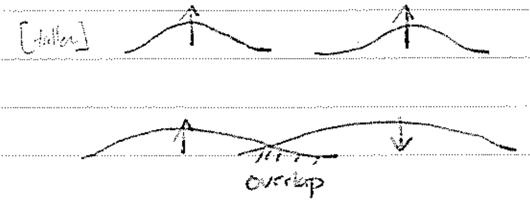
$$\mathcal{H} = -J \sum_{\langle ij \rangle}' \vec{s}_i \cdot \vec{s}_j \qquad \text{Heisenberg}$$

$\langle ij \rangle$: n.n. pairs



or $$\mathcal{H} = -J \sum_{\langle ij \rangle} s_i s_j \qquad \text{Ising}$$

Microscopic origin: Coulomb repulsion $\sim \frac{1}{R}$, R = typical (integrated) $e^- - e^-$ separation



Parallel spins: no overlap, large sepn → low pot energy

antiparallel: overlap → larger Coulomb rep. → high energy $\frac{e^2}{R}$

(Coulomb effect K ⋯

Heisenberg or even Ising hard to solve for usual reason — interacting system — while $\mathcal{H} = -B^{ext} \sum s_i$ is easy. Strategy: replace hard $\mathcal{H}$ with easy one. Instead of B^{ext}, use "effective" field B due to the averaged field contributions of all spins:

$$\mathcal{H} = -J \sum_{\langle ij \rangle} s_i s_j = -J \sum_i' s_i \tfrac{1}{2} \underset{\substack{\#\text{ n.n.} \\ \text{(same for every spin)}}}{z} \langle s \rangle + \underbrace{J \sum_{\langle ij \rangle} s_i (\langle s \rangle - s_j)}_{\text{fluctuation term: Throw away}}$$

$$\approx -B \sum_i' s_i$$

Plug back in form $\mathcal{M} = n\mu\langle s \rangle$ and λ

where $B = \frac{1}{2} J z \langle s \rangle = \lambda \mathcal{M}$, $\lambda = \frac{Jz}{n\mu^2}$

Solve model self-consistently:

$$\begin{tikzcd} \text{moments } \mu_i \arrow[r, bend left] & \text{field } B \arrow[l, bend left, "\text{(paramagnet)}"] \end{tikzcd}$$

Note: Only in the model does the spontaneous B align the other spins in a dipole-dipole interaction. In the microscopic model, this effect is very small.

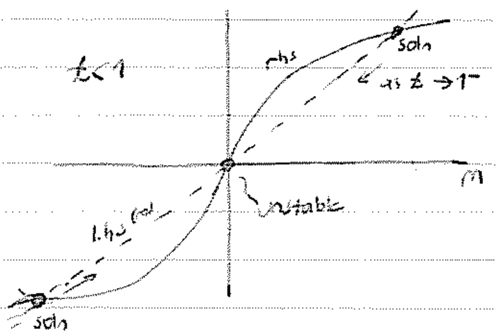
we've left off geometry & fluctuations

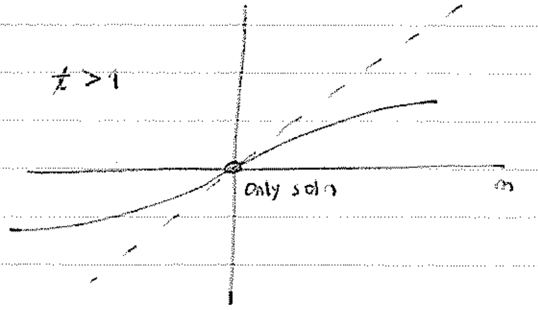
mean-field theory	Communism
μ_i	worker
B	the State
$\langle\mu\rangle$	ave. of all workers

$$\left.\begin{array}{lll} \text{so paramag.} & M = n\mu\tanh\left(\frac{\mu B}{k_B T}\right) \\ \text{mean field} & B = \lambda M \end{array}\right\} \longrightarrow M = n\mu\tanh\left(\frac{\mu\lambda M}{k_B T}\right)$$

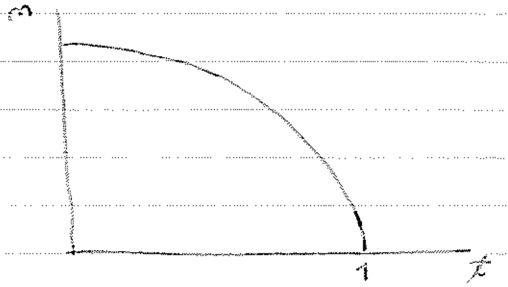
Introduce normalized variables $m = \frac{M}{n\mu}$, $t = \frac{k_B T}{n\mu^2\lambda}$: $\boxed{m = \tanh(m/t)}$

solve graphically





$t = 1$ is critical:



or, back to regular variables, $T_c = \frac{n\mu^2\lambda}{k_B}$

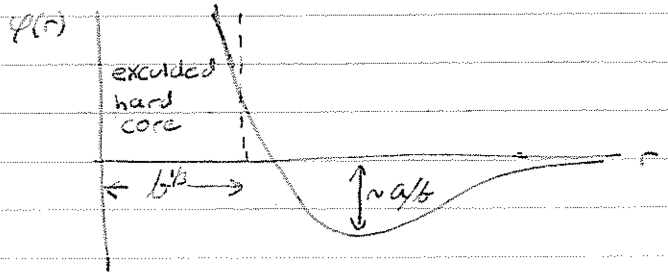
(Curie).

MFT: $\beta = 1/2$

actual: $\beta \simeq 0.325$

Back now to van der Waals – also a MFT

Instead of non-interacting gas, assume pair interaction



b: volume

a/b: energy

(One could derive from Lennard-Jones 6-12 potential.)
not necessary – we just need two phenomenological params, a & b

$$F^{ideal} = -Nk_BT\left[\ln(n_Q/n)+1\right]$$

First, replace $n = \frac{N}{V}$ with $n_{eff} = \frac{N}{V-Nb}$

Second, add another energy to F.

Estimate interaction energy for <u>one</u> <u>atom</u>: at $\vec{r}=0$

$$U_1^{int} = \iiint_{b^{1/3}}^{\infty} d^3r \; n(\vec{r})\,\varphi(r)$$

Concentration of atoms at $\vec{r}$: $n(\vec{r}) = \sum_{i\neq 0} \delta(\vec{r}-\vec{r}_i)$

Mean-field approximation: replace $n(\vec{r})$ with n so that every atom is the same:

$$U_1^{int} \approx n\int_{b^{1/3}}^{\infty} d^3r\;\varphi(r) \equiv -2na$$

Each worker interacts only with the state, and the state is the sum of all workers.

total interaction energy for all atoms

$$U^{int} = \frac{N}{2}U_1^{int} = -\frac{N^2a}{V}$$

Could [illegible] $V - Nb$, but [illegible]
[illegible]

Add U^{int} to the modified free energy.

$$F^{\text{vdw}} = -Nk_BT\left[\ln\left(n_Q(V-Nb)/N\right)+1\right] - \frac{N^2a}{V}$$

Pressure $$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = +\frac{Nk_BT}{V-Nb} - \frac{N^2a}{V^2}$$

3/3/01

$$\boxed{Nk_BT = \left(P + \frac{N^2a}{V^2}\right)(V-Nb)}$$

Contrast ideal $Nk_BT = PV$

$a, b = 0 \rightarrow$ ideal gas

Scaling: $P_c = \frac{a}{27b^2}$

$V_c = 3Nb$

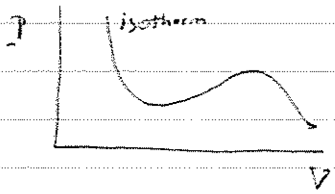
$T_c = \frac{8a}{27b}$

$$\boxed{\left(\frac{P}{P_c} + \frac{3}{(V/V_c)^2}\right)\left(\frac{V}{V_c} - \frac{1}{3}\right) = \frac{8}{3}\frac{T}{T_c}}$$

no params. left with respect to scaled variables $\frac{P}{P_c}$, etc.

Isotherms: show fig 10.10. Above T_c, no wiggle.
Compare to expt: Ar with fit for a, b at high T gives $T_c \rightarrow -119.7°C$, really $-122°C$

K+K don't do a good job of explaining fig 10.10 or its horizontal dashed lines.

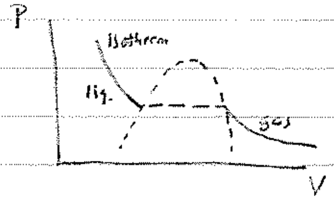


Peculiar that $P\uparrow$ as $V\uparrow$ with N fixed

more than peculiar: $\left(\frac{\partial F}{\partial V}\right)_{T,N} = -P$, so $\left(\frac{\partial P}{\partial V}\right)_{T,N} = -\left(\frac{\partial^2 F}{\partial V^2}\right)_{T,N}$,

but this must be NEGATIVE, else F not a minimum wrt V @ const. T, N

Compare to



At coexistence, $P_{gas} = P_{liq}$.

vdW unphysical $P(V)$ for part of range - really indicating coexistence, but where is line?

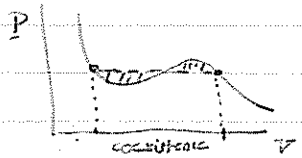
Maxwell construction:

recall $0 = SdT - VdP + Nd\mu$

On an isotherm, $dT = 0$, so

$$d\mu = \frac{V}{N}dP$$

$$\mu_\ell - \mu_g = 0 = \int_{gas}^{liq} d\mu = \frac{1}{N}\int_{gas}^{liq} VdP = 0 = \frac{1}{N}\Big[\overset{\text{rectangle}}{PV\Big|_{gas}^{liq}} - \int_{gas}^{liq} PdV\Big] \Rightarrow \text{Maxwell's "equal-area" rule}$$



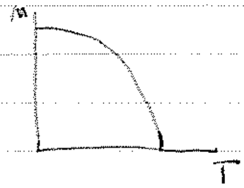
3/20/03 Wed.: mean-field theories:
Curie-Weiss ferromagnet
van der Waals

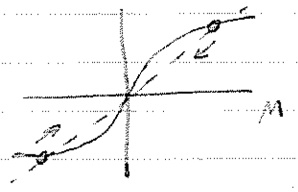
today: Landau theory
Start binary mixtures

Mon.: binary mixtures

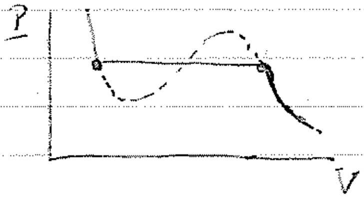
We saw two examples of how an analytic (differentiable, Taylor-expandable) func. could describe a transition in which s.t. was not differentiable:

1.





2.



This suggested to Landau a general framework:

1. Identify an <u>order parameter</u>, ξ

   e.g., m for FM
   superconducting/superfluid fraction
   fraction of A-B bonds in binary alloy
   $\lim_{n\to\infty}\int \rho(x)\rho(x+na)\,d^3x$ in solid (suitably normalized)

2. Write free energy as function of T & ξ (allowing latter to vary):

$$F_L(\xi, T) = U(\xi, T) - TS(\xi, T)$$

3. Variational method: minimize F_L w.r.t. ξ to find equilibrium value, $\xi_0(T)$
4. Form of F_L is chosen to give the kind of transition we want:
   - assumed analytic - Taylor expand about $\xi = 0$
   - coefficients constrained by $\boxed{\text{symmetry}}$ of problem

If there's a symmetry $+\xi \leftrightarrow -\xi$, as in Ising FM, F_L is even, and we can write

$$F_L(\xi, T) = g_0(T) + \tfrac{1}{2} g_2(T)\,\xi^2 + \tfrac{1}{4} g_4(T)\,\xi^4 + \tfrac{1}{6} g_6(T)\,\xi^6 + \dots$$

Fractions in front not important – K&K put them there in anticipation of taking a derivative. Other authors absorb them into the gs.

If we had any other knobs (e.g., ext. field, pressure), the gs would depend on them as well as on T.

To model a second-order transition, truncate after 4th term, set g_0, g_4 = constants (at least near transition temp), and let $g_2(T)$ be a monotonically increasing function: K&K write $g_2(T) = (T-T_0)\alpha$, $\alpha > 0$.

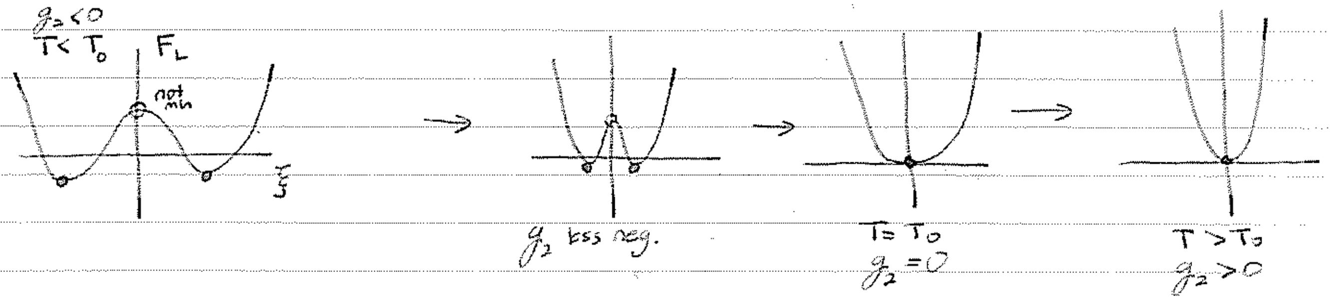
$$F_L(\xi, T) = g_0 + \tfrac{1}{2} g_2(T)\,\xi^2 + \tfrac{1}{4} g_4\,\xi^4$$

To find equilibrium $\xi = \xi_0(T)$:

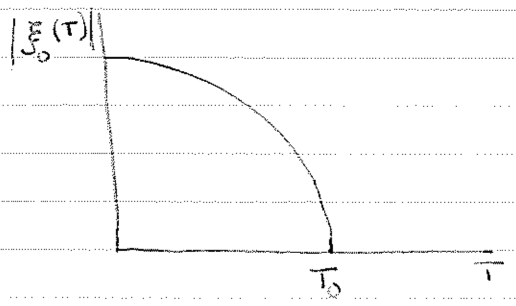
$$0 = \left(\frac{\partial F_L}{\partial \xi}\right)_T = g_2\,\xi + g_4\,\xi^3$$

roots: $\xi = 0$,
$\xi = \pm\sqrt{-g_2/g_4}$ (real root[s] only for $g_2 < 0$)

Successive graphs of F_L for increasing T:



This gives a 2nd-order transition:



Say we want a 1st-order transition – one way is to go to 6th order in ξ.

$$F_L(\xi, T) = g_0 + \frac{1}{2} g_2(T)\xi^2 - \frac{1}{4} g_4 \xi^4 + \frac{1}{6} g_6 \xi^6 \quad , \; g_4, g_6 > 0$$

$$0 = \frac{\partial F_L}{\partial \xi} = g_2(T)\xi - g_4 \xi^3 + g_6 \xi^5$$

$$\xi = 0$$

$$\text{or} \quad g_2(T) - g_4\xi^2 + g_6\xi^4 = 0$$

$$\rightarrow \quad \xi^2 = \frac{g_4 \pm \sqrt{g_4^2 - 4g_6 g_2}}{2g_6}$$

increase T ↓

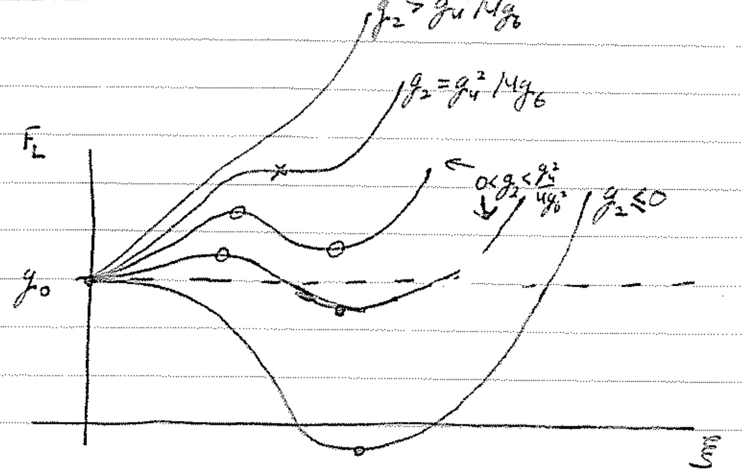
$g_2 < 0$: $\sqrt{} > g_4$, so only + root → real ξ

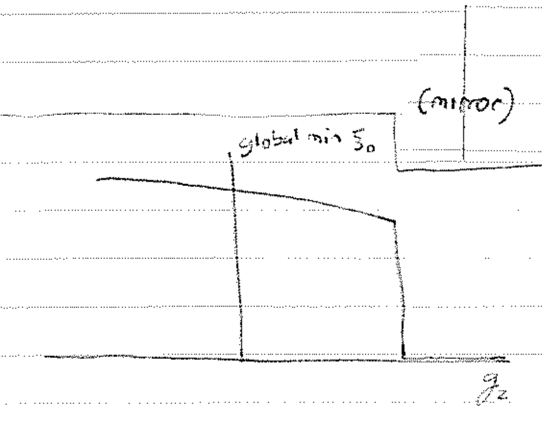
$g_2 = 0$: one (non-0) root for ξ^2

$0 < g_2 < \frac{g_4^2}{4g_6}$: two real roots – one is a max, one a min. (but may not be global min.)

$g_2 = g_4^2/4g_6$: one non-0 root for ξ^2

$g_2 > \frac{g_4^2}{4g_6}$: $\xi = 0$ only real root

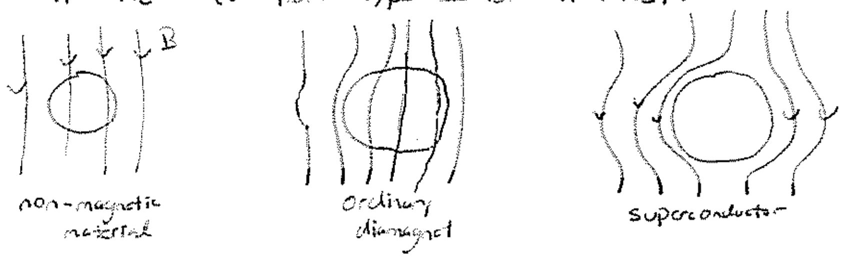




Problem 10.6

Use Gaussian units : $\mu_0 \to 4\pi$

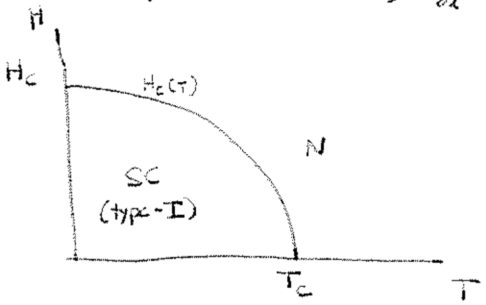
Meissner effect: magnetic flux expelled from a type-I superconductor for external field $H < H_c$ (or from type-II for $H < H_{c1}$)



perfect diamagnetism not just a consequence of perfect conductivity, which would give, via

$$\nabla \times E = -\frac{1}{c}\frac{\partial B}{\partial t}$$

perfect cond ⇒ $E = 0 \Rightarrow \frac{\partial B}{\partial t} = 0$ i.e., no change in flux



Large enough H destroys S.C. For $T < T_c$ and $H < H_c(T)$, S.C. has lower free energy than normal metal. At $H_c(T)$, free energies must be equal.

This gives a way to find the free-energy difference favoring s.c. at $H = 0$: it's the work required to expel flux at $H = H_c$.

free-energy difference at zero field $\Delta f = \frac{1}{V}(F_S - F_N) = -\frac{H_c^2(\tau)}{8\pi} < 0$ (uniform H)

$$\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_{V,N,H}$$

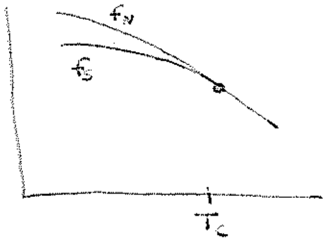
write $s = \sigma/V$

$$\Delta s = -\frac{d}{d\tau}(\Delta f) = \frac{1}{8\pi}\frac{d(H_c^2)}{d\tau} = \frac{1}{4\pi}H_c(\tau)\frac{dH_c}{d\tau}$$ negative, as in graph above

3rd law: $\lim_{\tau \to 0} \Delta s = 0$, so $\frac{dH_c}{d\tau} \to 0$: curve is horizontal at $\tau = 0$

b) (1) "merge" means not only are the free energies equal at T_c, but they also approach T_c with the same slope.

$\frac{d(\Delta f)}{d\tau}$ is just (minus) Δs, which vanishes at τ_c, so the free energies "merge:"



(from K&K)

(2) Since $\Delta(\tau_c\sigma) = 0$ and $\Delta f = 0$, $\Delta U = 0$.

(3) $\Delta(\tau_c\sigma) = 0$ means no latent heat at τ_c.

If $H \neq 0$, latent heat per unit volume $\tau|\Delta s| = \frac{\tau}{4\pi} H_c(\tau) \left|\frac{dH_c}{d\tau}\right|$.

3/18/02

c) $C_S - C_N = \Delta C$. Use $C_V = \tau\left(\frac{\partial s}{\partial \tau}\right)_{V,N,H}$.

$$\Delta C = \tau \frac{d}{d\tau} \Delta s = \frac{\tau}{8\pi} \frac{d^2(H_c^2)}{d\tau^2}.$$

If for $\tau \ll \tau_c$, $\Delta C \approx -C_N = -\gamma\tau$,

$$\gamma = -\frac{1}{8\pi} \frac{d^2(H_c^2)}{d\tau^2} \quad \text{(in limit } \tau \to 0\text{)}.$$

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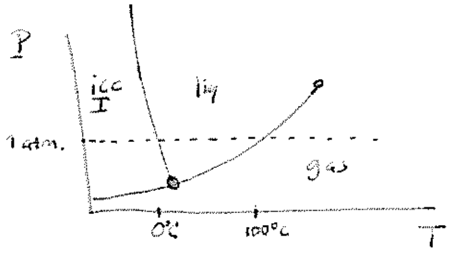
start 3/21/02

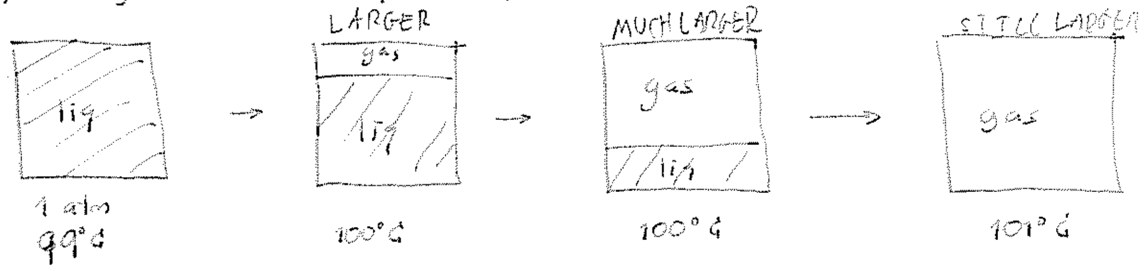
Back to H_2O.



At $P = 1$ atm., coexistence of liquid and gas only at 100°C. What about humidity?

This introduces two ideas: mixture (air = $N_2 + O_2 + \ldots + H_2O$) & partial pressure

The phase diagram above is for pure H_2O, no air:



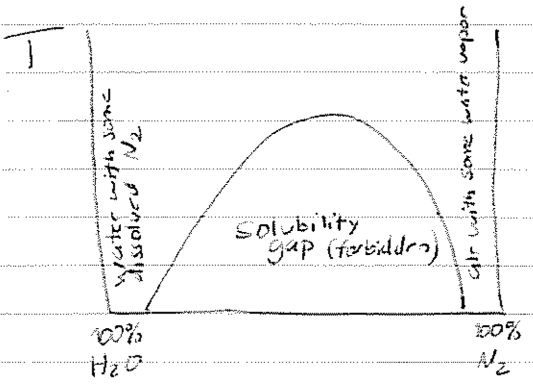
Volumes should increase progressively

whole thing in a cylinder capped by a piston to maintain P = 1 atm

However, with air supplying part of the pressure, the partial pressure of H_2O will be much lower → some "boils" (evaporates) even below 100° C

equilibrium = "100% saturation" = Florida in July

~~interfacial energy:~~
Story of Chapter 11 :



Made up solubility diagram of H_2O and N_2

competition between energy & entropy

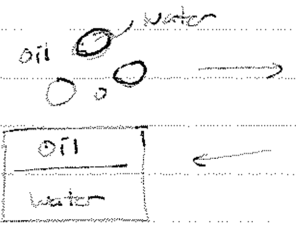
3/28/03

3/31/03 Fri: Phase transitions
example of type I superconductor
today: binary mixtures
wed. eutectics
start cryogenics
FINISH NOTES PAGES 112-113

Vinaigrette – salad dressing
1 part vinegar (balsamic or red wine)
2 parts oil (olive or walnut)
spices (mustard seed, basil leaf, etc.)
SHAKE

[illegible]

Simplified recipe :
oil
water
Shake → emulsion



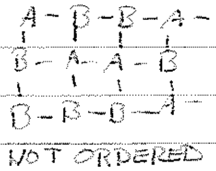
water-oil ~~interface~~ has higher energy than bulk water, so drops get bigger with time
(H_2O-H_2O dipole-dipole bond stronger than H_2O-oil)

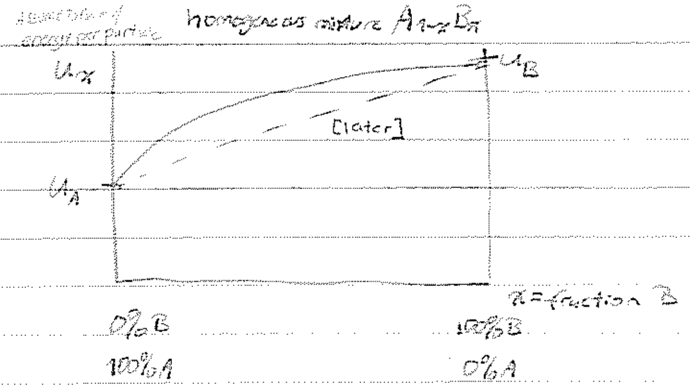
Maximize # water-water by minimizing surface area

CONTRAST:

energy per molecule in a <u>homogeneous</u> mixture (much finer than emulsion)

Schematic



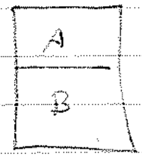


Energy of phase-separated combination:

$$= (1-x)\,u_A + x\,u_B \longrightarrow$$ ADD DASHED LINE TO GRAPH

connects lower [illegible] [illegible] phase sep at T = 0

Book leaves off interface energy from →



estimate magnitude compared to interface energy in 50%-50% homogeneous mixture:

in latter, $\sim \frac{1}{2}$ all bonds are AB

total # bonds $\sim 6 \cdot \frac{N}{2} = 3N$

$N = N_A + N_B$ = total # ~~[illegible]~~

replace 6 w/ true # n.n. if not NaCl structure

area $\sim 100\,\text{cm}^2$

$\Rightarrow$ height $\sim 10\,\text{cm}$

How high is monolayer? Say $\rho \sim 1\,g/cc$ (water)

$$m_{H_2O} \sim 18\,\text{amu} = 18\left(\frac{5}{3}\cdot 10^{-24}\,g\right)$$

$$\sim 30 \cdot 10^{-24}\,g$$

If cubic, lattice constant $\sim \sqrt[3]{\dfrac{30\cdot 10^{-24}\,g}{1\,g/cc}}$ (treat 30 like 27)

$$= 3 \cdot 10^{-8}\,\text{cm}$$

So fraction of height ~ fraction of AB bonds $\sim 3\cdot 10^{-9}$ negligible

which is why ~~K~~ & K neglect it

Things do mix even if energetically disfavorable: ENTROPY of mixing.

A, B metals (PV negligible, so we'll minimize F instead of G)

homogeneous $A_{1-x}B_x$ or phase separation

PHASE SEPARATED FIRST:

If A, B have same bulk structures, $S_A = S_B \Rightarrow (1-x)S_A + x S_B \equiv S_0$ present whether phase segregated or not

Even if structures differ, the entropies will be comparable — we'll assume equal

Entropy of mixing in homogeneous mixture only:

N atoms
$N_B = xN$ of these B
$N_A = (1-x)N$ are A

multiplicity
$$g = \binom{N}{N_B} = \frac{N!}{N_A!\,N_B!} = \frac{N!}{([1-x]N)!\,(xN)!}$$

$$S'_M = k_B \ln g = k_B\left[\ln N! - \ln\left(((1-x)N)!\right) - \ln\left((xN)!\right)\right]$$

$$\approx k_B\left[N\ln N - N - (1-x)N\ln([1-x]N) + (1-x)N - xN\ln(xN) + xN\right]$$

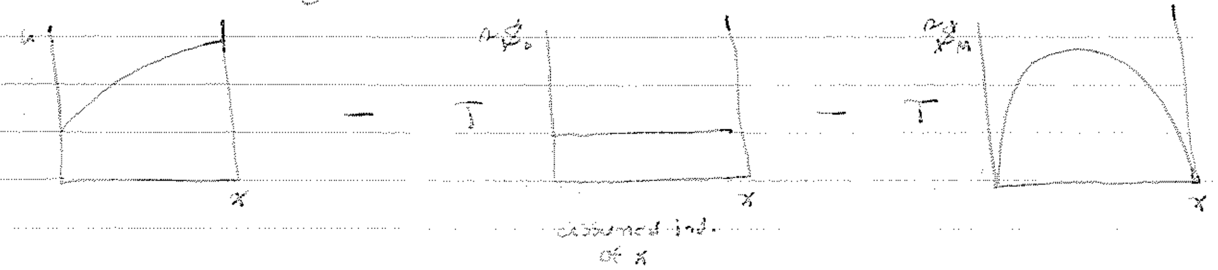
$$= k_B\left[\underline{N\ln N} - \underline{N} - (1-x)N\ln(1-x) - (\underline{1}-\underline{x})N\ln N + (\underline{1}-\underline{x})N - xN\ln x - \underline{xN\ln N} + \underline{xN}\right]$$

$$= Nk_B\left[(x-1)\ln(1-x) - x\ln x\right]$$

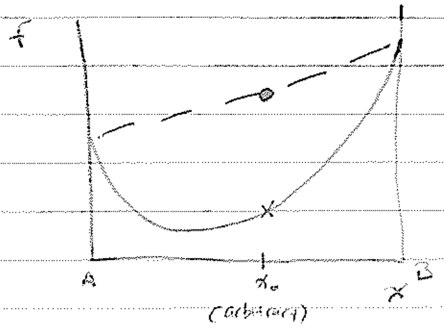
This term absent in phase-segregated configuration.

$\sigma_0 = S_0/N$; $\sigma_M = S_M/N$

Total free energy/atom $f = u - T\left[\tilde{\sigma}_0 + \tilde{\sigma}_M\right]$



At high enough T, f is dominated by $-TS_M$:



Homogeneous mixture (——) has lower f even though higher u than phase segregated config. (– – –) – for any x

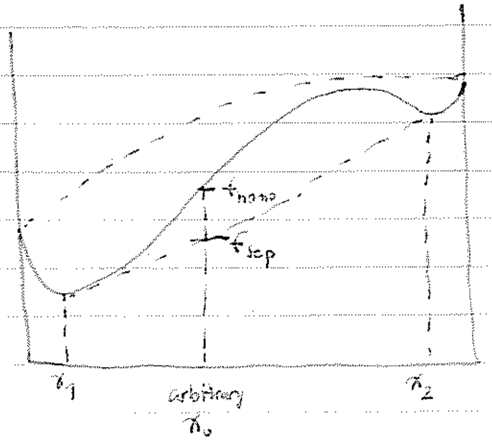
So A & B are miscible at this temp.

At low temp., S_M still important at edges because of ∞ slope:

put the prefactor back! (still ∞)

$$\left.\frac{dS_M}{dx}\right|_{x=0} = \lim_{x\to 0} -Nk_BT\frac{d}{dx}x\ln x = -\lim_{x\to 0} Nk_BT(\ln x+1) = +\infty$$

$$\left.\frac{dS_M}{dx}\right|_{x=1} = \lim_{x\to 1} Nk_BT\frac{d}{dx}(x-1)\ln(1-x) = \lim_{x\to 1} Nk_BT\left[\ln(1-x)+\frac{x-1}{1-x}\right] = -\infty$$



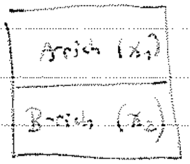
(upper) – – : not incl entropy of mixing, s_M

——— : including s_M

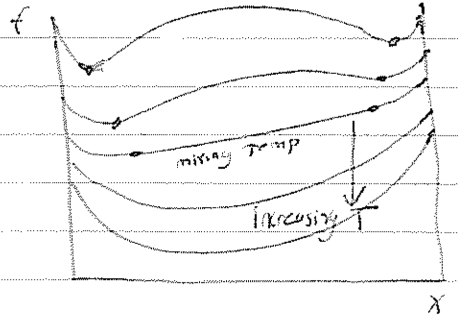
For $0 \le x \le x_1$, homogeneous mixture $A_{1-x}B_x$ has lowest f. Similarly for $x_2 \le x \le 1$. However, between x_1 & x_2, mixture separates into two phases

A-rich $A_{1-x_1}B_{x_1}$ not pure A

& B-rich $A_{1-x_2}B_{x_2}$ not pure B

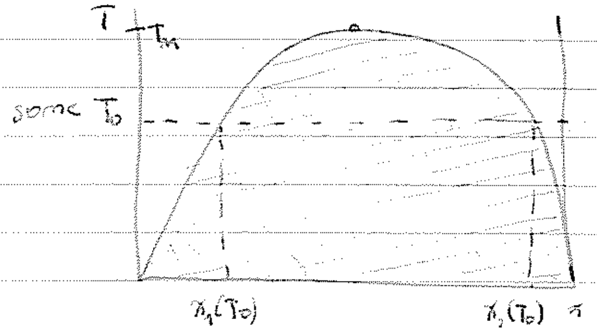


x_1 & x_2 are NOT minima, rather, tangent points family of curves



[Not quite right, tangent pts. need to meet at mixing temp]

→ Solubility gap



no homogeneous mixtures (alloys) in forbidden region

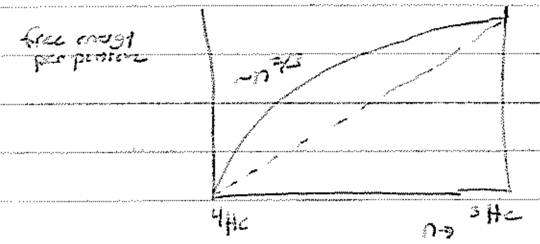
4/2/03 Mon.: entropy of mixing
phase separation
today: phase separation
eutectics
start cryogenics
Fri.: cryogenics

[last two graphs]

^3He - ^4He mixture has similar solubility gap but for a different reason. I don't think there's much in the way of He - He energy, much less a difference among u_{33}, u_{34}, and u_{44}. Superfluid ^4He at low T ($T_{BCS,\,^3He} < T \ll T_{\lambda,\,^4He}$) contributes almost no energy, so look at ^3He:

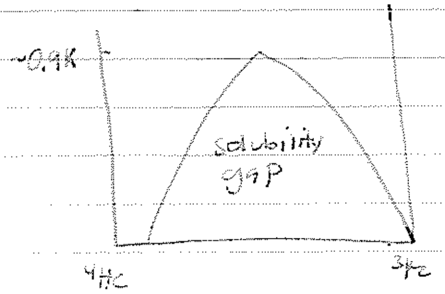
$$\text{Fermi gas} \quad \frac{U_0}{V} = \int_0^{\varepsilon_F} d\varepsilon\, \varepsilon\, g(\varepsilon) \sim \int_0^{\varepsilon_F} d\varepsilon\, \varepsilon^{3/2} \sim \varepsilon_F^{5/2}$$

$$\varepsilon_F \sim n^{2/3}, \text{ so } \frac{U_0}{V} \sim n^{5/3}, \text{ or } \frac{U_0}{N} \sim \frac{V}{N} n^{5/3} = \boxed{n^{2/3}}$$



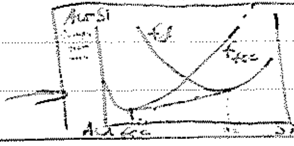
So even without any bond energy, we still get the right curvature.

Entropy-of mixing argument proceeds as normal



Technological application for Fridge or Mandy:
dilution refrigerator

3/31/04



x_1 is almost pure Au

x_2 almost pure Si

come back to this system after discussing liquid-solid equilibrium

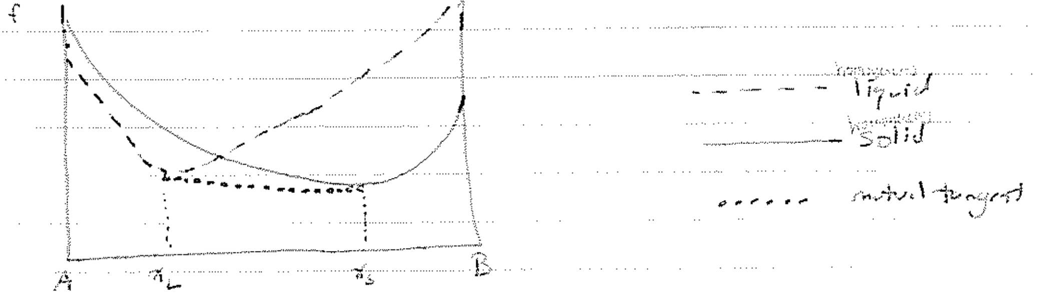
Melting of mixture with no solubility gap (e.g., Si-Ge)

assumptions for simple model:

- no solubility gap for either liquid or solid mixtures
- melting temps. $T_A < T_B$

For $T > T_B \to$ homogeneous liquid
$T < T_A \to$ homogeneous solid

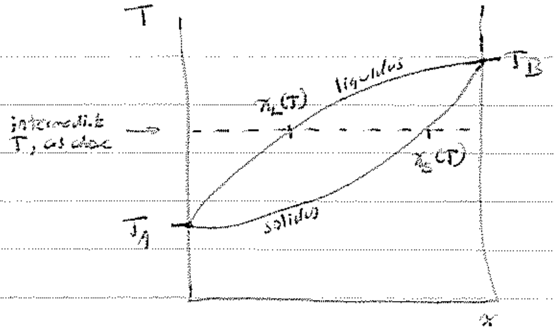
At some temperature $T_A < T < T_B$ so pure A is liquid, pure B solid:



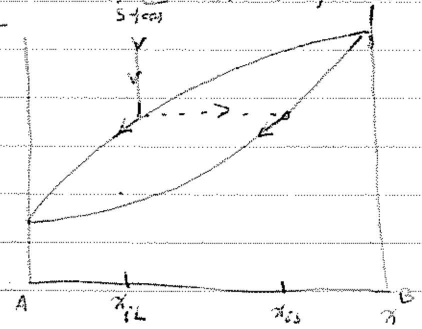
$x < x_L$: homogeneous liquid $A_{1-x} B_x$

$x > x_S$: homogeneous solid $A_{1-x} B_x$

Considering family of curves such as above,



Mixture does not solidify @ one temp. but over a range: when we hit liquidus,

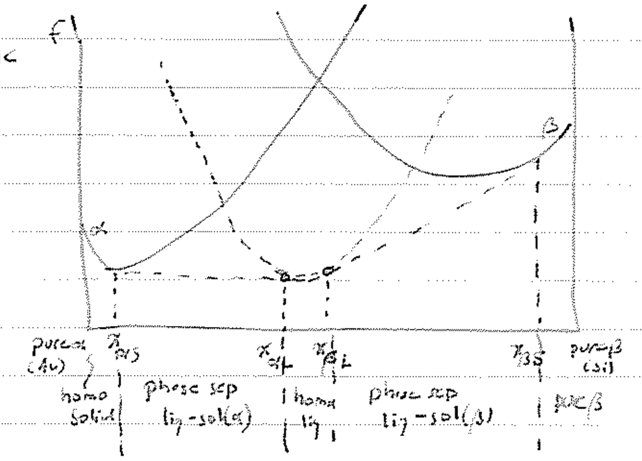


a precipitate forms not at x_{iL} but at x_{is}, depleting the B component and leaving the liquid more A-rich, so it solidifies at a lower temperature, etc. Solidification is not complete until T_A.

How can a binary mixture have a melting temp. that's lower than that of either of its constituents?

Au - Si system - differs from Si - Ge in having a solubility gap in the solid (only).

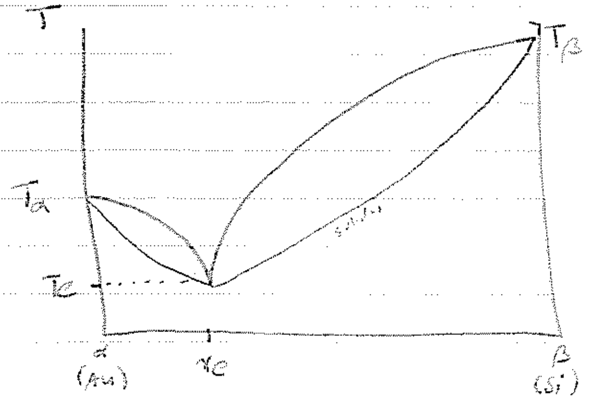
Schematic



[min of liquid could be lower]

—— solid: two branches because two diff. xtal structs. (fcc vs. dia)

- - - - liquid (no structure)



Eutectic mixture:

At Te, x_e, $x_{\alpha L} = x_{\beta L}$

If we start w/ liquid @ x_e & lower the temp, it solidifies suddenly at Te (@ like a pure material).

At any other x_0 ($\neq 0, 1$), it solidifies over a range of temps, as in previous model. Application: solder.

4/2/03 Wed.

Practical cryogenics

(warning: it's been a while since I worked in a low-temp lab, so who knows?)

Down to (maybe) ~50K? – closed cycle refrigerator

[of course, liquifiers go further]$\to$ 4.2K – may it be cost effective?

77K: boiling pt. of liquid N_2 at room pressure
plus heater to go above

rule of thumb: liq. N_2 costs per volume same as milk

4.2K: boiling of ^4He
can get down to ~1K by evaporative cooling
called "pumping on it"
maybe twice as far (0.5K) pumping on ^3He, but very expensive, so
need closed cycle

rule of thumb: costs same as whiskey

millikelvins: dilution refrigerator

below: $\nearrow$ nuclear demagnetization
(small samples) $\to$ laser cooling
(gases)

Show Jeff Olson's paper on low-T thermal conductivities (back spam)

4/4/03 Wed.: eutectics
cryogenics
today: cryogenics
Joule expansion
Joule-Thomson effect
dilution refrigerator
Mon.: laser cooling

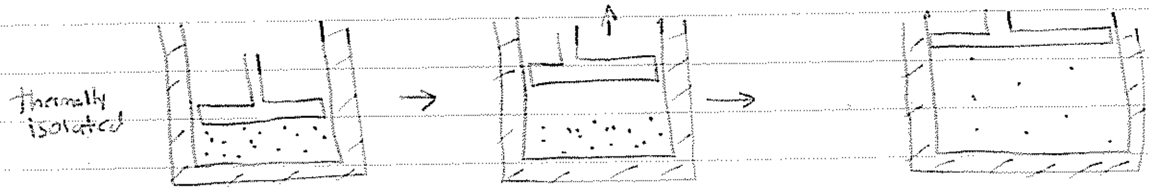
Show simplified schematic of cryostat

(some recent designs omit ℓ-N_2 stage)

reflective radn shielding
long path for tubes

Reversible refrigeration becomes difficult at low temp, particularly when the working fluid would liquify during the adiabatic-expansion stage, so for practical reasons, we're drawn to irreversible processes.

Joule effect - sudden (not isentropic) expansion, revisited



Irreversible. recall for ideal gas, no change in temp., since $U = \frac{3}{2}Nk_BT = U(T)$ only.

More generally, $U = U(T, V)$.

We can still use equilibrium thermodynamics, as the initial and final states are (separately) equilibria. I.e., $U(T,V)$ is an equilibrium func - don't care how we get from one state to another.

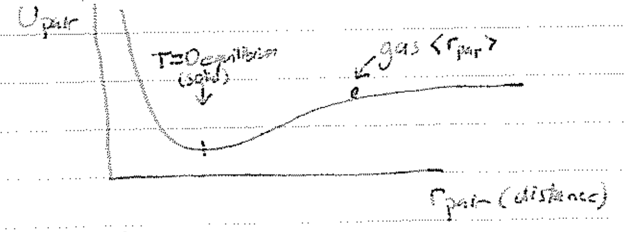
$$dU = 0 = \left(\frac{\partial U}{\partial T}\right)_V dT\Big|_U + \left(\frac{\partial U}{\partial V}\right)_T dV\Big|_U$$ ~ indicate constant U

$$\text{so} \quad \left(\frac{\partial T}{\partial V}\right)_U = -\frac{(\partial U/\partial V)_T}{(\partial U/\partial T)_V}$$

$$\text{denominator}: \left(\frac{\partial U}{\partial T}\right)_V = C_V, \quad \text{so}$$

$$\boxed{\left(\frac{\partial T}{\partial V}\right)_U = -\frac{(\partial U/\partial V)_T}{C_V}}$$

- Numerator always positive for gas:



so $\left(\frac{\partial T}{\partial V}\right)_U < 0 \Rightarrow$ expansion COOLS an interacting gas

4/2/03

Evaluate numerator: recall from ch. 3 (3.50) (lecture p25, 1/24/03)

$$P = -\left(\frac{\partial U}{\partial V}\right)_T + T\left(\frac{\partial S}{\partial V}\right)_T$$

$$\text{so numerator} = \left(\frac{\partial U}{\partial V}\right)_T = P - T\underbrace{\left(\frac{\partial S}{\partial V}\right)_T}_{\left(\frac{\partial P}{\partial T}\right)_V}$$

Maxwell relation

Thus $$\boxed{\left(\frac{\partial T}{\partial V}\right)_U = \frac{1}{C_V}\left[P - T\left(\frac{\partial P}{\partial T}\right)_V\right]}$$

Ideal gas : $P = \frac{Nk_BT}{V}$, so $T\left(\frac{\partial P}{\partial T}\right)_V = P \Rightarrow \overset{\text{why?}}{\cancel{\left(\frac{\partial U}{\partial V}\right)_T = 0}}$.

$\left(\frac{\partial T}{\partial V}\right)_U = 0$ (ideal gas) ~ as we knew before

non-ideal gas:

$$P = \frac{Nk_BT}{V}\left[1 + \frac{B_2(T)}{V} + \frac{B_3(T)}{V^2} + \ldots\right]$$ called virial or Kammerling-Onnes expansion

$B_2 = B_3 = \ldots = 0$ for ideal gas

Can calculate $B_i(T)$ for non-ideal gases – examples: van der Waals, Bose, Fermi

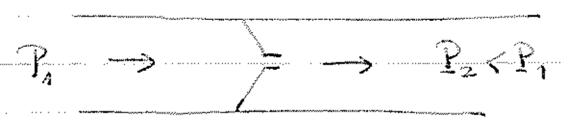
$P(T, V)$ is a Laurent rather than a Taylor expansion, because P blows up at $V = 0$.

If $\frac{B_3}{V}$, etc. are negligible (expected at low density, $\frac{N}{V} \ll n_Q$)

$$T\left(\frac{\partial P}{\partial T}\right)_V = \frac{Nk_BT}{V}\left(1 + \frac{B_2}{V} + \frac{T}{V}\frac{dB_2}{dT}\right) = P + \frac{Nk_BT^2}{V^2}\frac{dB_2}{dT}$$

so $$\boxed{\left(\frac{\partial T}{\partial V}\right)_U = -\frac{1}{C_V}\frac{Nk_BT^2}{V^2}\frac{dB_2}{dT}}$$ called "Joule" effect

Similar, more useful:



equivalently, porous, resistive partition

again, irreversible, but now we control pressure instead of volume – more suitable for a continuous process of liquifaction

$$\Delta U = U_2 - U_1 = P_1 V_1 - P_2 V_2$$

we assume no heat loss (I don't mean no heat from friction)

& ignore kinetic energy of fluids
(center of mass)

$$\underbrace{U_1 + P_1 V_1}_{} = \underbrace{U_2 + P_2 V_2}_{}$$

enthalpies equal $H_1 = H_2$

intuition:

$$V \longleftrightarrow P$$

$$\text{constant } U \longrightarrow \text{constant } H$$

so guess
$$\boxed{\left(\frac{\partial T}{\partial P}\right)_H = -\frac{1}{C_p}\left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right]}$$

Good guess except sign (so fix sign)

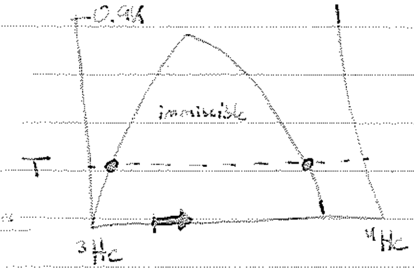
called Joule – Thomson effect (Thomson = Lord Kelvin)

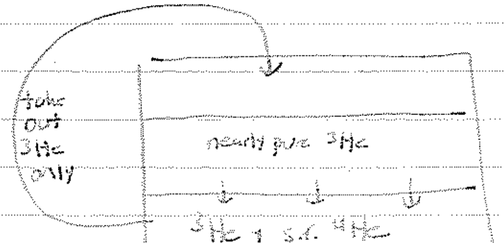
Unlike Joule expansion, sign depends on T.
For any gas, there's an inversion temperature below which this cools, above which it heats, so in liquifaction it's first necessary to cool below inversion temperature.

[illegible]

Dilution refrigerator:

fundamental idea: ^{3}He gives up heat faster dissolving into ^{4}He than evaporating into vacuum.





"evaporation" is down, not up

GO THROUGH DIAGRAM, P344

2007: [illegible]

Historically important cooling method: Pomeranchuk effect

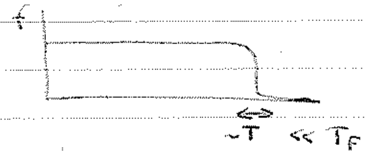
Used by Lee, Osheroff, Richardson in 1972 to form superfluid ^3He

review by Bob Richardson in his 1996 Nobel lecture
RMP 69 683 (1997)

Compress solidifying ^3He

At low T,
entropy of solid > entropy of liquid, so it takes heat to solidify → liquid cools

even normal ^3He a quantum liquid
so only a small proportion
of states are available for entropy

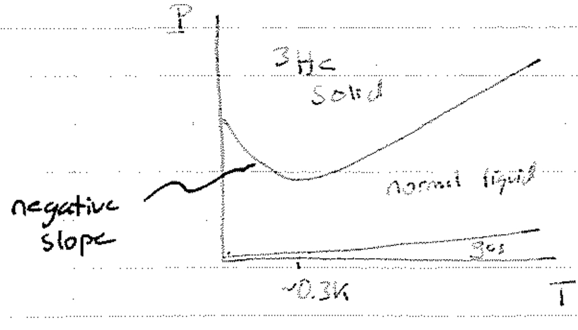


[illegible] /
normal liquid [illegible] solid, on
the other hand, has spin [illegible]
degrees of freedom.

Clausius - Clapeyron

$$\frac{dP}{dT} = \frac{s_{liq} - s_{solid}}{v_{liq} - v_{solid}} = \frac{\overset{\text{negative}}{\text{latent heat per molecule}}}{\underbrace{T}_{\text{small positive}}\underbrace{(v_{liq} - v_{solid})}_{\text{positive}}}$$

so $P\uparrow \to T\downarrow$



(superfluid phase below ~2.5 mK)

superfluidity in ^3He a consequence of Cooper pairing, similar to superconductivity

refer to Osheroff's review in same issue of RMP - calling advisors at 4:00 AM
(picture)

4/4/10

condensates:

Bosonic : ^4He — strongly interacting — superfluid Kapitza, 1938
$T_c \sim 2.1\ K$

atomic BEC, e.g., Rb — weakly or non interacting U. Philips says yes (~~probably not superfluid~~ ?) 1995
$T_c \sim 2\mu K$
(hard part is density)

paired Fermions:

usual type-I s.c. (e.g., Pb)	s-wave ($l=0$)	$T_c = 7.2K$	BCS
usual type-II s.c. (e.g., Nb_3Sn)	s-wave ($l=0$)	$T_c = 18.3K$	BCS
heavy-Fermion type II s.c. (eg, UPt_3)	s-wave ? + p-wave Sr_2RuO_4	$T_c = 0.533K$	?
^3He - A ^3He - B	p wave ($l=1$)	$T_c \approx 2.5mK$ see p. 211	BCS
high-T_c s.c. (e.g., $Tl_2Ba_2Ca_2Cu_3O_{10}$)	d-wave ? ($l=2$) some admixture ?	$T_c \sim 125K$	?

The "Bosons" are of course also grouped Fermions — There are theories that interpolate.

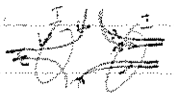
4/7/03 Fri.: dilution refrigerator
today: condensates
laser cooling & trapping — can only give a flavor
Wed.: kinetic theory

Phillips, RMP 70 721 (1998)

useful ref. Raab et al. PRL 59 2631 (1987) (Chu)

ingredients in optical cooling:

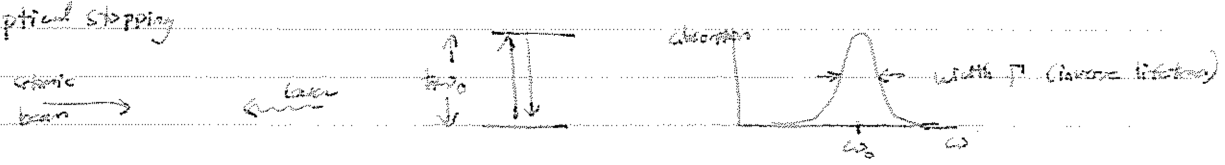
0. Magnetic trap — anti-Helmholtz



+ uniform

somehow (?) $3S_{1/2}$ state cares about $|B|$, not $\vec{B}$ — drawn to minimum @ center

1. optical stopping



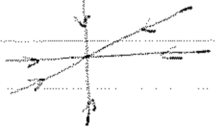
subtleties: won't work very far because of
1) Doppler shift (explain)
2) hyperfine splitting of ground state

#2 dealt with by second beam to pump atoms out of unwanted level

#1: Use spatially modulated magnetic field to cancel Doppler with Zeeman

— this just about stops the beam

2. Doppler cooling: "optical molasses"



x, y, z beams (6)

$\omega_{laser} = \omega_0 - \delta$

$\delta = \Gamma/2$ turns out to be optimal

Atom absorbs more strongly from beam toward which it is headed — momentum transfer slows it down regardless of direction

force on atom $\vec{F} \sim -\alpha \vec{v}$ (for small v → blue shift < δ)

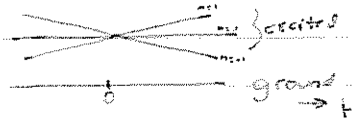
resulting velocity distribution nearly Maxwellian, so T is well defined

Doppler → ~200μK (competition from laser heating ← random recoil)

2′ sub-Doppler cooling: Stark shift in $\overset{\text{modulated (circ. polarized)}}{\text{electric}}$ field → 50μK see Cohen-Tannoudji's Nobel lecture

2″ magneto-optical trap

see Raab



much stronger than magnetic trap above

polarized light to conserve angular momentum

incorporates Doppler

3. evaporative cooling → 50nK

reduce trapping pot'l enough so highest-energy — hottest — atoms leave but cold atoms stay

discuss picture of velocity distrib'n

adiabatic demagnetization — refer to book

4/9/03 Mon.: Bose-condensed atomic gases

today: example problem Ch.12

Kinetic theory

Fri.: diffusion

correct misprint on the assignment 13

Problem 12.4

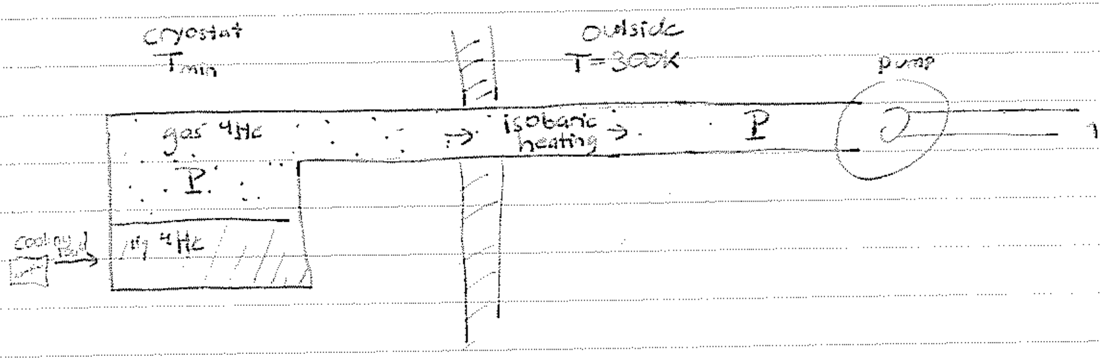
At steady state, we're removing heat at rate $q = L_0 S'$

S' = effective pump speed at interface

L_0 = latent heat per mole = 82 J/mole

table 12.1

assumed ind. of T (~~i.e. P~~)



Ignoring any resistance to flow, pressure same until pump (less at pump if there is resistance) – steady state same as equilibrium except for center-of-mass flow and lack of energy transfer backward

effective pump speed $S' = \frac{\#\text{moles}}{\text{sec}}$. S given in $\frac{\text{vol}}{\text{time}}$ at ~~1atm~~ P – use ideal-gas law to convert

see p.417 (table) - so we must correct to get #moles

$$= S \cdot \frac{1\text{ mole}}{24\ell} \frac{P}{\underset{\underset{760\text{ torr}}{\approx}}{1\text{ atm}}} = \alpha S P, \quad \alpha = \frac{\text{mole}}{24\ell\ 760\text{ torr}}$$

$$q = L_0 S' = L_0 \alpha S P$$

$$P = \frac{q}{L_0 \alpha S} = 0.22 \text{ torr}$$

Show graph of fit:

$P(T) = P_0 e^{-L_0/(k_B T)}$

so

$\ln P = \ln P_0 - \frac{L_0}{k_B} T$

hardly differs from interpolation

Interpolate in table 12.2 : T between 0.98 and 1.27

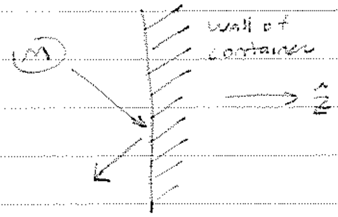
$0.22 = 10^{-0.65}$, so $T \approx 0.65 \cdot (0.98\text{K}) + 0.35 (1.27\text{K}) = \boxed{1.1\text{ K}}$

Classical kinetic rederivation of ideal-gas law

Recall, first, derivation in Ch. 3 & 6 – outline

1. Quantum concentration n_Q – set by assuming negligible occupancy ≥ 2, so we never find out if we're Fermi or Bose – "I have some marbles – how many ways are there to put them in boxes?" same as "I have some boxes – what occupation numbers are possible?"
2. Non-interacting gas: $Z = n_Q V$
3. $\lambda = n/n_Q$ (fugacity)
4. $\mu = k_B T \ln(n/n_Q)$
5. $\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} \overset{\text{integrate}}{\Rightarrow} F = N k_B T \left[\ln\left(\frac{n}{n_Q}\right) - 1\right]$
6. $P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{N k_B T}{V}$

Kinetic theory – classical way of getting pressure



momentum change of wall due to one collision $= 2M|v_z|$.

There are many collisions. Let $\rho(v_z)\,dv_z$ be prob. for a particle to have velocity between v_z and $v_z + dv_z$.

n = concentration

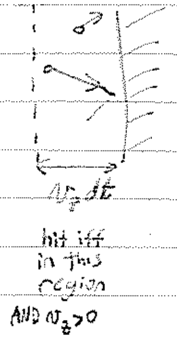
$n\rho(v_z)\,dv_z$ = # particles per unit volume w/ z-velo. between v_z and $v_z + dv_z$

$$\text{force} = \frac{\text{mom. change}}{\text{unit time}} = \frac{\text{\# that hit wall}}{\text{unit time}} \cdot 2M|v_z|$$

of course, will need to integrate over v_z

$$\text{pressure} = \frac{\text{force}}{\text{unit area}} = \frac{\text{\# hit}}{\text{area} \cdot \text{time}} \cdot 2M|v_z|$$

So how ~~many~~ many will hit wall in time dt? First, consider only particles with v_z between v_z and $v_z + dv_z$ …



$$\frac{\#\text{ hit}}{\text{unit area}} = n\rho(v_z)\,dv_z\,v_z\,dt$$

divide by dt to get $\frac{\#\text{ hit}}{\text{unit area}\cdot\text{time}}$

$\rightarrow$ pressure due to v_z = $2Mn\,v_z^2\,\rho(v_z)\,dv_z$

Now integrate over all $\overset{\text{positive}}{\wedge}$ v_z:

$$P = \int_0^\infty 2Mn\,v_z^2\,\rho(v_z)\,dv_z = Mn\int_{-\infty}^{\infty} v_z^2\,\rho(v_z)\,dv_z$$ since v_z as likely as $-v_z$

$$= Mn\langle v_z^2\rangle$$

ave. energy per particle $\frac{U}{N} = \frac{1}{2}M\langle v^2\rangle = \frac{1}{2}M\langle v_x^2 + v_y^2 + v_z^2\rangle$

$$= \frac{3}{2}M\langle v_z^2\rangle$$ one direction as good as another

$P = \frac{2}{3}\cdot\overbrace{\frac{N}{V}}^{n}\cdot\frac{U}{N} = \frac{2}{3}\frac{U}{V}$. If we assume equipartition, $U = \frac{3}{2}Nk_BT$,

we have $\boxed{P = \frac{Nk_BT}{V}}$

4/7/04 4/10/05

We've cheated, since thus far our discussion of equipartition has been quantum-mechanical. Outline of purely classical argument (see Feynman, vol I):

1. TD def'n of temp. by heat engines
2. when two gases can exch. energy, kinetic energy $\overset{\text{of molecules}}{\wedge}$ of the two species equal: $\langle KE_1\rangle = \langle KE_2\rangle$
3. Define $T \propto \langle KE\rangle$
4. Show equivalence of definition #3 & def'n #1.

4/13/07

Maxwell's velocity distribution

Only QM input will be that accessible states are distributed uniformly in momentum, $\vec{p}$.

We're essential doing the reverse of what we did to derive $g(E)$ (but hiding the quantization of $\hbar k$).

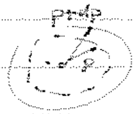
$\underline{P}(p_x, p_y, p_z)$ = prob. $\overset{\text{density}}{\wedge}$ particle has momentum $\overset{p_x,\ p_y,\ p_z}{\text{~~between~~}}$ ~~p_x and $p_x + dp_x$~~
~~p_y and $p_y + dp_y$~~
~~p_z and $p_z + dp_z$~~

$$= \frac{e^{-\beta(p_x^2+p_y^2+p_z^2)/(2m)}}{\int dp_x\, dp_y\, dp_z\, e^{-\beta(p_x^2+p_y^2+p_z^2)/(2m)}}$$

$$\text{denom} = \left(\int dp_x\, e^{-\beta p_x^2/(2m)}\right)^3 = (2\pi m k_B T)^{3/2}$$

$$\text{so } \underline{P}\, dp_x\, dp_y\, dp_z = \frac{e^{-\beta p^2/(2m)}}{(2\pi m k_B T)^{3/2}}\, dp_x\, dp_y\, dp_z \qquad p^2 = p_x^2+p_y^2+p_z^2$$

fraction of states between p & $p+dp$ $\sim p^2$



$$\underline{P}\, dp = \frac{e^{-\beta p^2/(2m)}\, 4\pi p^2\, dp}{(2\pi m k_B T)^{3/2}} = \frac{e^{-\frac{1}{2}mv^2\beta}\, 4\pi m^2 v^2 m\, dv}{(2\pi m k_B T)^{3/2}}$$

Should be called "Maxwell speed distribution" – equivalent distribution of velocities, $\vec{v}$, is just ordinary gaussian.

$$= 4\pi\, e^{-\frac{1}{2}mv^2\beta} \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2\, dv \qquad \text{agrees w/ K\&K 14.11}$$

Why no $\hbar$ in this deriv'n as in K&K?

We've hidden $g(E)$ in the assumption that states uniform in $\vec{p}$ (or $\vec{k}$) space – we don't have to count them, because they cancel $\frac{\text{numerator}}{\text{denominator}}$.

$$\text{Applications:} \quad \sqrt{\langle v^2 \rangle} = \sqrt{\int dv\, v^2\, \underline{P}(v)} = \sqrt{\frac{3 k_B T}{m}} \qquad \text{problem 14.1}$$

Note that $\overset{\equiv \langle|\vec{v}|\rangle}{\langle v \rangle}$, $\sqrt{\langle v^2 \rangle}$, and v^* (most probable) are all different.

$\langle \vec{v} \rangle = 0$, of course, is still different.

Alternative derivation:

$$P_E(E)g(E)\,dE = \alpha\, e^{-\beta E} \underbrace{E^{1/2}}_{\sqrt{\frac{m}{2}}v} \underbrace{dE}_{mv\,dv} = P_v(v)\,dv$$

quantum state

$$\text{so } P_v(v)\overset{dv}{=} \alpha\, e^{-\beta E}\, m^{3/2}\, 2^{-1/2}\, v^2\, dv$$

α ind. of v. get it by requiring normalization

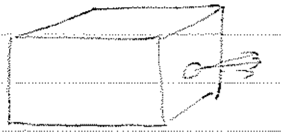
4/11/03 Wed.: $PV = Nk_BT$

Maxwell velo. dist $\sim v^2 e^{-\frac{1}{2}mv^2}$

~~today~~: diffusion

Mon. ~~Fri.~~: Boltzmann equation

Exp't verification of Maxwell velo. distribution:



KBK point out that there's an extra factor of v for particles that actually escape, so $P_{beam} \propto v^3 e^{-\frac{1}{2}mv^2}$

Mean free path:

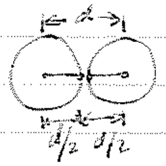
transport in gas: molecules move $\boxed{\text{ballistically}}$ until they collide; afterward, directions are random

mean free path l: average distance between collisions; $l = \bar{c}\tau_0$

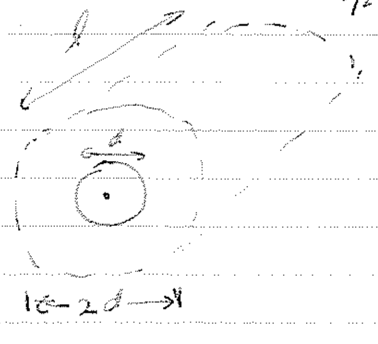
$\bar{c}$ = average speed ($\neq v_{rms}$?)

τ_0 = relaxation time (or mean free time)

rigid-sphere model:



collide if they're within d of each other



Moving molecule sweeps out path of volume $\pi d^2 l$ in sense that it will collide w/ any other molecule whose centre is in this volume.

Want on ave. 1 other molecule in this volume for l to be m.f.p.

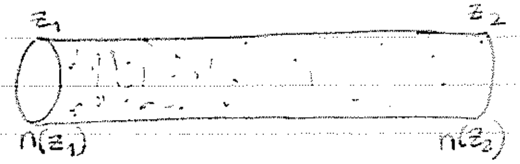
concentration $n = \frac{1}{\pi d^2 l}$, or $\boxed{l = \frac{1}{n\pi d^2}}$

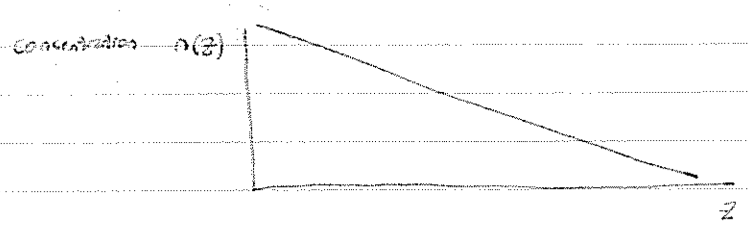
linear response: response of dissipative system is linear in some gradient

some examples (table 14.2)

field	response	
temp T	heat flow $\vec{J}_u = -\kappa \nabla T$	
elec. pot V	current density $\vec{J}_q = -\sigma \nabla V = \sigma \vec{E}$	(Ohm's law)
particle conc. n	number flux $\vec{J}_n = -D \nabla n$	

Start with particle diffusion.





Assume T same on both sides so that avg. KE and so speed of particles ind. of z

Fick $\vec{J}_n = -D\nabla n$ Units: n: cm^{-3}

J_n: s^{-1}cm^{-2} $\vec{\nabla} n$ points left

D: cm^2/s

rationalization : or $\frac{1}{n}, \frac{1}{n^2}, \ldots$

no constant term because $n=0 \Rightarrow$ no flux

no $n, n^2, \ldots$ because no difference in $n \Rightarrow$ no net flux

∇n makes sense because it measures difference in n

no $\nabla^2 n$, etc. because "less" local $\nabla^2 n$ would tell us about sound propagation – distinguishes local and nonlocal mes:

[illegible] no $(\nabla n)^2, (\nabla n)^3, \ldots$ etc. – small for small enough ∇n, and also nonlinear | we expect no flux in either case

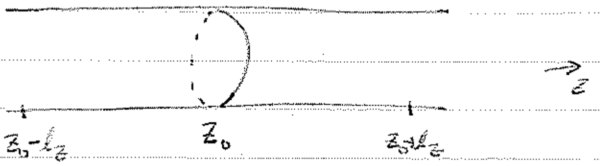
$\to n\nabla n$: & other nonlinear terms quadratic in n – implausible

we expect $J \propto n$: double the density, double the flux

This leaves Fick's law.

Joke about "WKB"

Calculation will put this on perhaps firmer ground and also estimate D in terms of Maxwell velo. distribution & frequency of collisions.



flux through plane = right-moving flux − left-moving flux

right flux : proportional to • density n
- and to a mean speed c_z in z direction
- factor of $\frac{1}{2}$ because only $\frac{1}{2}$ of particles move to right
- What is c_z ? Ave z proj. of velo. only of those particles that move to the right
- where is density n? Not at $z=z_0$ but to the left of it by l_z, z proj. of MFP, since density there determines flux at z_0.

l_z & c_z are correlated, so it does not make sense to use the value of $\bar{c}_z$ derived in problem 14.1
$= \langle c_z \rangle$

i.e., $\langle l_z \rangle \langle c_z \rangle \neq \langle l_z c_z \rangle$. We'll need the latter.
For now leave l_z & c_z. We'll take the average later.

Right flux $= \langle \frac{1}{2} n(z-l_z)\, c_z \rangle$
left flux $= \langle \frac{1}{2} n(z+l_z)\, c_z \rangle$

total flux $J_n = \langle \frac{1}{2} c_z \underbrace{\left[n(z-l_z) - n(z+l_z) \right] \cdot \frac{2 l_z}{2 l_z}} \rangle$

$$\downarrow$$

$-\frac{dn}{dz}$ if $l_z \ll$ length scale of interest

$J_n = - \langle c_z l_z \rangle_{\substack{\text{right} \\ \text{moving}}} \frac{dn}{dz}$ ave. is over only forward directions; we've already account left as −right

$c_z = |v| \cos\theta$ $\xrightarrow{\ \theta\ } z$

$l_z = t_0 |v| \cos\theta$ t_0 = relaxation time $= \frac{\ell}{[illegible]|v|}$ $\ell =$ mfp, $\bar{c} = \langle |v| \rangle$

really $t_0 = \ell / \bar{c}$?

$\langle c_z l_z \rangle = \frac{\lambda}{[illegible]} \left\langle \frac{2\pi \cdot \int_0^{\pi/2} \sin\theta\, d\theta (|v| \cos\theta)^2 / |v|}{2\pi \int_0^{\pi/2} \sin\theta\, d\theta} \right\rangle_{\text{maxwell}}$, $\langle \cdot \rangle_{\text{maxwell}} = \int_0^\infty dv\, (\cdot)\, P_{\text{max}}(v)$

Angular & Maxwell averages separate: $\langle |v| \rangle_{\text{Maxwell}} = \bar{c}$, so

$$\langle c_z l_z \rangle = l\bar{c}\,\frac{\int_0^{\pi/2} d\theta \sin\theta \cos^2\theta}{1} = -l\bar{c}\,\frac{1}{3}\cos^3\theta\Big|_0^{\pi/2} = \frac{1}{3} l\bar{c}$$

$$\boxed{J_n = -\frac{1}{3}\bar{c}l\,\frac{dn}{dz} \equiv -D\,\frac{dn}{dz}}$$

so $D = \frac{1}{3}\bar{c}l$ in kinetic model

More generally, $\vec{J} = -D\vec{\nabla}n$

$$\boxed{\frac{\partial n}{\partial t}} = -\nabla\cdot J$$ explain – continuity eqn – apply Gauss's thm

$$= \boxed{D\nabla^2 n}$$ diffusion equation

contrast wave eqn., which has 2nd time derivative

Similar for thermal diffusion:

$n(z) \to \rho_E(z)$ energy density (i.e., erg/cm³)

For solid, energy would be carried by phonons.
Assume instead a gas with densities balanced
so that there's no net flow of particles, only of
energy (more complicated if both particles & heat diffuse).

To simplify expressions, use $n^+ = n(z+l_z)$, $n^- = n(z-l_z)$, $c_z^+ = c(z+l_z)$, etc.

Energy flux to right $= \frac{1}{2} n^- c_z^- \cdot \frac{3}{2} k_B T^-$
to left $= \frac{1}{2} n^+ c_z^+ \cdot \frac{3}{2} k_B T^+$

I've assumed a near-ideal gas (monatomic) –
never truly ideal, because w/o collisions
there's no energy xport

particle flux to right $= \frac{1}{2} n^- c_z^-$
to left $= \frac{1}{2} n^+ c_z^+$
} sum = 0, so write $n^- c_z^- = n^+ c_z^+ = nc_z$

Net energy flux $J_u = \frac{1}{2} n c_z \cdot \frac{3}{2} k_B \underbrace{(T^- - T^+)}_{-2l_z \frac{dT}{dz}} = -nc_z l_z \frac{3}{2} k_B \frac{dT}{dz}$. Use $c_z l_z = \frac{1}{3}\bar{c}l$

$= -\frac{1}{2} n k_B \bar{c} l \frac{dT}{dz}$, so

$$\boxed{J_u = -K\frac{dT}{dz}}$$ with $K = \frac{1}{2} n k_B \bar{c} l = \frac{1}{3} c_V \bar{c} l$ where $c_V = \frac{C_V}{V} = \frac{3}{2} n k_B$

4/14/03 Fri. diffusion
today: diffusion
Boltzmann eqn.
Wed.: modern critical phenomena

From Fri.: $J_u = -\kappa \nabla T$, $\kappa = \frac{1}{2} n k_B \bar{c} \ell = \frac{1}{3} c_v \bar{c} \ell$, $c_v = {C_V}/{V}$, $\bar{c} = \langle |v| \rangle$

How does κ depend on concentration (equiv. on pressure)?

$c_v \sim n$

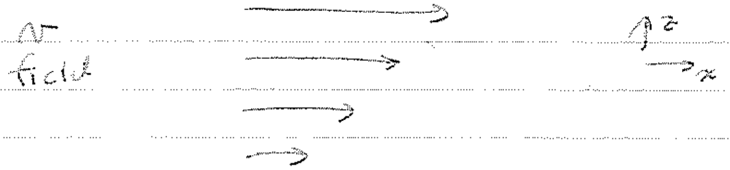
$\ell \sim 1/n$ result from Fri.

So κ ind. of n (or at fixed T of P)

partial vacuum conducts heat exactly as well as room-pressure air: fewer particles to carry heat, but each one moves further before scattering. Effects cancel. This picture breaks down only when $\ell \sim$ physical dimensions $= \ell_{max}$. Then $\kappa \approx \frac{1}{3} c_v \bar{c} \ell_{max}$. As we lower pressure further, ℓ_{max} doesn't increase (how could it?), but c_v gets smaller — "Knudsen regime."

[illegible]

viscosity:



Friction carries a momentum in the $-z$ direction (explain).

$$\boxed{J^{z}_{p_x} = -\eta \frac{dv_x}{dz}}$$

For a more general treatment (3-dim flow, mom.) see L&L Fluid Mechanics.

Result from K&K for gas: $\eta = \frac{1}{3} \rho \bar{c} \ell$, ρ = mass density

4/17/03

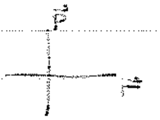
[Away from equilibrium:]

Boltzmann eqn. (really strategy more than eqn.)

— concerns distribution function in single-particle, semiclassical phase space, $f = f(\vec{r}, \vec{p}, t)$ t = time

and its equilibrium value

$f_0(\vec{r}, \vec{p})$

Particles have trajectory in 6-dim space. (1-dim analogue: )

— In words:

(l.h.s.) f changes due to (r.h.s.) the things that change f

— model: relaxation time t_0 (τ_c in K&K, but I called it t_0 last week)

— two sorts of things changing:

1. particle moves in phase space: $\vec{r} = \vec{r}(t)$, $\vec{p} = \vec{p}(t)$
2. $f(\vec{r}, \vec{p}, t)$ may itself depend on t

Think of driving around on landscape in which hills, valleys, etc. change fast rubber

Starting point:

$$\frac{\partial f}{\partial t} = \left(\frac{\partial f}{\partial t}\right)_{\text{collisions}} + \left(\frac{\partial f}{\partial t}\right)_{\text{flow}} + \left(\frac{\partial f}{\partial t}\right)_{\text{fields}}$$

↳ everything else

note: 1) subscripts here are not like $\left(\frac{\partial \cdot}{\partial \cdot}\right)_{T,V}$ but are still essential

2) l.h.s. represents change in f at fixed point $\vec{r}, \vec{p}$ in phase space — we could call it $\left(\frac{\partial f}{\partial t}\right)_{\vec{r}, \vec{p}}$. In fluid dynamics, $\frac{df}{dt}$ (full derivative)
is reserved for the value of $f(\vec{r}(t), \vec{p}(t), t)$ following some particle in the fluid.

First, the collision term.

Relaxation-time approximation: fraction scattering in time dt is $\boxed{\frac{dt}{t_0}}$

Scattering erases memory of $\vec{p}$

To compute fraction scattering in a non-infinitesimal time t,
write $t = N\delta t$ and take limit $\delta t \to 0$, $N \to \infty$, preserving t.

Fraction <u>not</u> scattered in time δt is (in limit) $1 - \delta t / t_0$.

Fraction not scattered in time t is

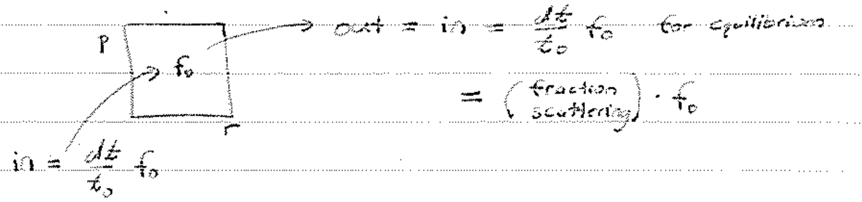
$$\left(1 - \frac{\delta t}{t_0}\right)\left(1 - \frac{\delta t}{t_0}\right)\cdots\left(1 - \frac{\delta t}{t_0}\right)$$

For simplicity, we've assumed t_0 ind. of t.

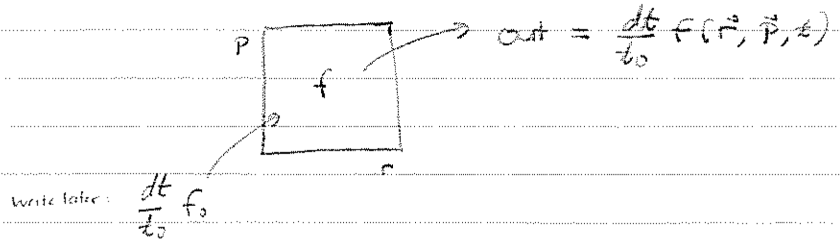
$$= \left(1 - \frac{\delta t}{t_0}\right)^N \underset{\lim}{=} e^{-t/t_0}$$

(e.g. by Taylor series)

Consider first a small piece of phase space at equilibrium:



Now consider non-equilibrium distribution:



Relaxation-time approximation says that collisions erase memory of previous non-equilibrium distribution, so incoming is <u>again</u> $\frac{dt}{t_0} f_0$ (DRAW).

Net: $\left(\frac{\partial f}{\partial t}\right)_{coll} = \frac{1}{t_0}(f_0 - f)$

f relaxes exponentially toward f_0 in absence of other terms:

Write $\eta(r, p, t) = f(r, p, t) - f_0(r, p)$

$$\left(\frac{\partial \eta}{\partial t}\right)_{coll} = -\frac{1}{t_0}\eta$$

$$\Rightarrow \eta(t) = \eta(0)\, e^{-t/t_0}$$

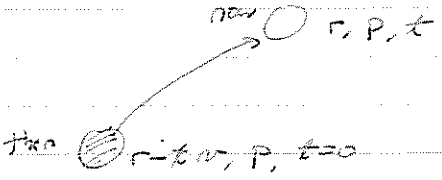
Flow term. Absent collisions and fields, particle moves with constant $\vec{p}$

(Corpus omne perseverare in statu ... &c.)

$$f(r, p, t) = f(\vec{r} - t\vec{v}, \vec{p}, t=0)$$

In words: to figure out what's going on at r, p at time t, look back at $r - vt$, p at time 0.

Picture:



Note: $\vec{v} = \vec{p}/m$.

~~Final term: Let $\vec{F}$ be force due to external.~~

Take time derivative.

$$\left(\frac{\partial f}{\partial t}\right)_{\text{flow}} = -\frac{\partial f}{\partial \vec{r}} \cdot \overset{\vec{v}}{\cancel{\frac{d\vec{r}}{dt}}} = -(\vec{\nabla}_r f) \cdot \vec{v}$$

The minus sign is confusing — those who've studied fluid dynamics recognize it as the convective derivative.

Final term: Let $\vec{F}$ be force due to external field (e.g., $\vec{F} = q\vec{E}$).

Newton's second law: $\vec{F} = \frac{d\vec{p}}{dt}$

$\vec{F}$ changes $\vec{p}$ and only indirectly affects $\vec{r}$

$$f(r, p, \delta t) = f\left(r, p - \delta t \frac{d\vec{p}}{dt}, 0\right) \quad + \text{ non-field terms}$$

Pick δt small enough that $\frac{dp}{dt}$ constant between 0 and δt.

$$\left(\frac{\partial f}{\partial t}\right)_{\text{fields}} = -\frac{\partial f}{\partial p}\frac{dp}{dt} = -(\nabla_p f) \cdot \vec{F}$$

Putting together the 3 terms:

$$\frac{\partial f}{\partial t} = \frac{1}{t_0}(f_0 - f) - (\nabla_r f) \cdot v - (\nabla_p f) \cdot F$$

K&K use v instead of p; other authors use k

Use the formalism to rederive $J = -D\nabla_r n$, $D = \frac{1}{3}\bar{c}\ell$

No external field $(F=0)$. As before, for simplicity take $\nabla_r = \partial/\partial z$.
In steady state $\frac{\partial f}{\partial t} = 0$, so Boltzmann reads

$$\boxed{\frac{1}{t_0}(f_0 - f) = v_z \frac{\partial f}{\partial z}}.$$

$$\text{so} \quad f = f_0 - v_z t_0 \left(\frac{\partial f}{\partial z}\right)_p$$

$$\simeq f_0 - v_z t_0 \left(\frac{\partial f_0}{\partial z}\right)_p$$

If we need a better approximation, plug this in for f on the r.h.s. of the previous line:

$$f \simeq f_0 - v_z t_0 \left[\left(\frac{\partial f_0}{\partial z}\right)_p - v_z t_0 \left(\frac{\partial^2 f_0}{\partial z^2}\right)_p\right] \qquad \text{etc.}$$

Justification for using 1st order: small perturbation ⇒ small $f - f_0$ (linear response). v_z already small

$$\text{flux } J = \underset{\text{spinless}}{\int} \frac{d^3k}{(2\pi)^3} f(p(k))\, v_z \qquad \vec{p} = \hbar\vec{k} = m\vec{v}$$

$$\simeq \underbrace{\int dk_x\, dk_y\, dk_z \cdot \frac{1}{(2\pi)^3} f_0\, v_z}_{0 \text{ since}} - \int \left(\frac{\partial f_0}{\partial z}\right)_p v_z^2\, t_0\, dk_x\, dk_y\, dk_z$$

$f_0 = f_0(\mathcal{E}) = e^{(\mu - \mathcal{E})\beta} = f_0\left(\frac{\hbar^2 k^2}{2m}\right)$ is even in k_z, while

$v_z = \frac{\hbar k_z}{m}$ is odd. physically, no flux in equilibrium

To evaluate second integral, note $\left(\frac{\partial f_0}{\partial z}\right)_p = \left(\frac{\partial f_0}{\partial \mu}\right)_p \frac{d\mu}{dz} = \beta f_0 \frac{d\mu}{dz}$

Two choices: 1) assume t_0 ind. of $\vec{k}$ (i.e., of $\vec{v}$) so that it comes out.

2) Assume ℓ ind. of $\vec{k}$, $\ell = \langle t_0(k)\, v\rangle$, or $t_0 = \ell/v$
before average

These give answers that differ by ~5%. Solid state convention #1, kinetics of gases #2.

Which is right? Neither — collisions are more complicated than model. Both treat t_0 (or ℓ) as a phenomenological parameter.

Pick #2.

Then

$$J = -\frac{d\mu}{dz}\,\ell\beta\int\frac{v_z^2}{v}f_0\,\frac{d^3k}{(2\pi)^3}$$

1. $\dfrac{d\mu}{dz} = \dfrac{d}{dz}\left[k_BT\ln\left(\dfrac{n}{n_Q}\right)\right]$. Only n depends on z, so

$$= k_BT\,\frac{1}{n}\,\frac{dn}{dz}.$$

Note n_Q is necessary, but Boltzmann didn't need to know what it was, since it dropped out.

2. write $v_z^2 \rightarrow \frac{1}{3}v^2$, $\rightarrow$ integral $= \frac{1}{3}\int|v|f_0\,\frac{d^3k}{(2\pi)^3} \equiv \frac{1}{3}n\langle|v|\rangle$

$$\equiv \frac{1}{3}n\bar{c}$$

Then $J = -\frac{1}{3}\cancel{k_BT}\,\frac{1}{\cancel{n}}\,\frac{dn}{dz}\,\ell\cancel{\beta}\,\cancel{n}\,\bar{c}$

$$= -\frac{1}{3}\ell\bar{c}\,\nabla n = -D\nabla n \qquad \text{with } D = \frac{1}{3}\ell\bar{c}$$

4/16/03 Mon: Boltzmann

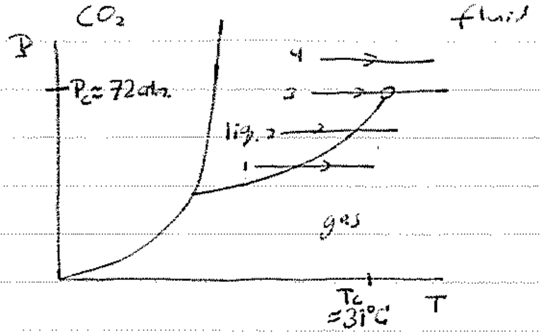
today: critical exponents

Fri: renormalization group

(finish pp. 149–150)

Critical Phenomena

References:
- M.E. Fisher's lectures at summer school, Univ. of Stellenbosch, Jan. 1982
  in F.J.W. Hahne, ed., Critical Phenomena, Springer 1983
- Nigel Goldenfeld, Lectures on Phase Transitions & the Renormalization Group
- Julia Yeomans, Statistical Mechanics of Phase Transitions



observations on coexistence line:

1: boiling – two coexisting fluids, each transparent (diff. densities, refractive indices) – latent heat

2. same – difference in densities less, smaller latent heat

4. no discontinuous change in appearance or density, no coexistence, no latent heat

---

3. $T < T_c$ transparent

$T > T_c$ transparent.

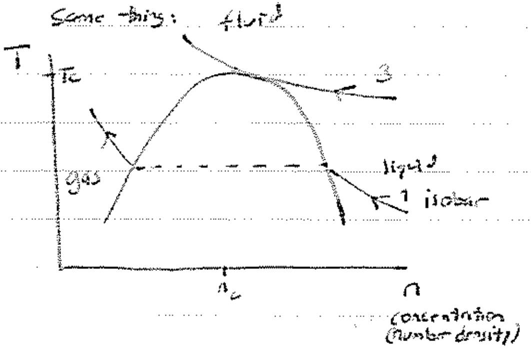
$T \cong T_c$ critical opalescence : forward scattered light brownish-orange
"streaky" "like a sunset on a smoggy day"
Side scattered: bluish
[like atmosphere but immensely stronger]

no latent heat

(Photo)

4/M04

Same thing:



Universality: plot $\frac{T}{T_c}$ vs. $\frac{n}{n_c}$ for various systems – they all coincide near the critical point

examples: $\underbrace{CO_2,\ Ar,\ Kr,\ N_2,\ O_2}_{\text{Simple fluids ~~gases~~ for which vdW serves well (away from crit. pt.)}},\ \underbrace{H_2O}_{\text{Chemically complex}},\ \underbrace{{}^3He,\ {}^4He}_{\text{quantum fluids (Fermi/Bose)}}$

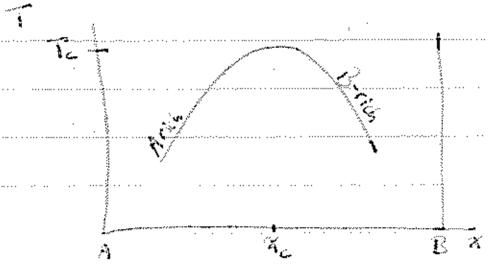
Inference: microscopic differences among fluids not in play – something is happening on a length scale large enough to scatter visible light (~0.5μ)

Quantitatively: define $\boxed{\text{reduced temperature}}$ $t = \frac{T - T_c}{T_c}$. Then at crit. pt.

$$n_{liq} - n_{gas} \sim |t|^{\beta} \quad \text{as } T \to T_c^- \text{ along coexistence line}$$

β same for the examples, in range 0.32–0.34 ($SF_6 : \beta = 0.327(6)$; $^3He : \beta = 0.321(6)$).

Universality extends to a very different system, the binary mixture of Ch. 11:



$x_{B\text{-rich}} - x_{A\text{-rich}} \sim |t|^{\beta}$ as $t \to 0^-$ $(T \to T_c^-)$

same β as before for CCl_4/C_7F_{14}

At first, Na/Li/Cs dissolved in NH_3 look different, with β apparently $1/2$. However, for $|t| < 0.003$, again $\beta \simeq 0.33$

size of "critical region" not universal; outside crit. region MFT $\overset{\text{may}}{\text{holds}}$

4/16

Definition of "$\sim$":

$$f(x) \sim x^{\lambda} \quad \text{as } x \to 0^{\pm}$$

means $\displaystyle\lim_{x \to 0^{\pm}} \frac{\ln(f(x))}{\ln x} = \lambda$ graphically: slope of log-log plot

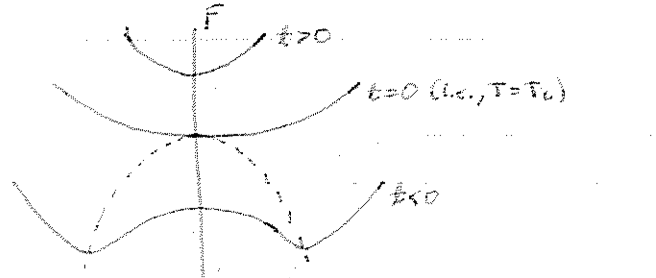
e.g., $f(x) = A x^{\lambda}$: $\displaystyle\lim_{x \to 0^{+}} \frac{\ln A + \lambda \ln x}{\ln x} = \lambda$

This also works if there are log or other corrections, e.g.,

$$f(x) = A x^{\lambda} |\ln x|^{\mu}$$

$$\lim_{x \to 0} \frac{\ln A + \lambda \ln x + \mu \ln|\ln x|}{\ln x} = \lambda$$

Landau theory for β:



ξ for fluid could be $\dfrac{n_{liq} - n_{gas}}{n_c}$ negative just reverses roles

[illegible]

$$F = F_0 + \tfrac{1}{2} g_2(t)\, \xi^2 + \tfrac{1}{4} g_4\, \xi^4$$

spontaneous order at minima

$$\frac{dF}{d\xi} = g_2(t)\,\xi + g_4\,\xi^3 = 0 \quad :$$

$$\xi = 0 \text{ or } \xi = \pm\sqrt{-g_2/g_4}$$

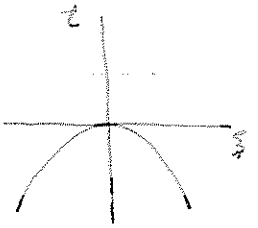
Assume $g_2(t)$ can be Taylor-expanded about $t=0$, where g_2 changes sign:

$$g_2(t) = 0 + at + 0 + bt^3 + \cdots$$ only odd so it changes sign

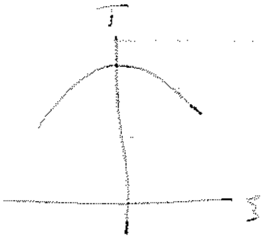
$$\approx at$$ close enough to $t=0$

$a > 0$

so $\xi^2 = \frac{-at}{g_4}$



or



$$+\xi - (-\xi) = 2\xi = 2\sqrt{\frac{a}{g_4}}\,|t|^{1/2} = \text{const.}\,|t|^{1/2}$$

so $\beta = 1/2$ in disagreement with experiment

Landau theory equiv. to MFT: both ignore spatial fluctuations away from equilibrium

---

Examples of critical exponents:

single-component order param, $d=3$

call it ξ to avoid confusion w/ order param

		MFT	RG
	$C_V(t) \sim \lvert t\rvert^{-\alpha}$	0	0.11
isothermal susceptibility	$\chi = \lim_{H\to 0^+}\left(\frac{\partial M}{\partial H}\right)_T = t^{-\gamma}$	1	1.23
correlation length ~~[illegible]~~	$\xi \sim t^{-\nu}$	1/2	0.63
	$n_{liq} - n_{gas} \sim \lvert t\rvert^{\beta}$	1/2	0.32

Relations (examples)

α, γ same above and below critical point

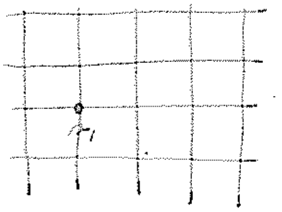
$\alpha + 2\beta + \gamma = 2$ Essam-Fisher

$\nu d = 2 - \alpha$ "hyperscaling" (d = dimensionality)

4/18/03 Wed.: Boltzmann → Fick
Critical phenomena
today: Critical phenomena
⋮
RG ?
next week: review

Model system: Ising

e.g., 2dim



Spin $s_i = \pm 1$

$$\mathcal{H} = -J\sum_{\langle ij\rangle} s_i s_j - H\sum_i s_i - NG$$

n.n.

H external field – we'll be interested in $H=0$
constant $-NG$ changes nothing but might be handy later

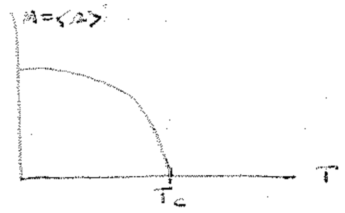
1D fairly easy
2D solved exactly by Lars Onsager 1944-1949 (chemist)
3D proven(?) NP-complete (Sorin Istrail 2000 ~~published but not citations?~~ ~~(stat? cosmologist)~~)
(this was just an extension to other 3D lattices)
F. Barahona J Phys A 15 3241 (1982) showed NP-complete

"Solved exactly" means expressions for free energy per spin $f(T)$, energy $u(T)$, specific heat etc. — closed form except for some simple integrals.
All the critical exponents can be calculated from the exact solution

2D
[illegible]

Phase transition at temp. $T_c \approx 2.269 J \overset{\text{exact}}{=} \frac{2}{\ln(1+\sqrt{2})}$ where 2.269 calculated to arb. precision

$T < T_c$: spontaneous magnetization
$T > T_c$: no net magnetization



$M \sim |t|^\beta$
For 2D Ising, $\beta = 1/8$ (exact)   3D : $\beta \approx 0.32$

Recall MFT in Ch. 10 of KBK :

$$m = \tanh(m/t') \ , \quad m = \frac{M}{M(0)} \ , \quad t' = \frac{T}{T_c} = t + 1$$

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$m = \tanh\left(\frac{m}{t'}\right)$, $\frac{m}{t'}$ is small near crit pt. so long as $T_c > 0$

$\approx \frac{m}{t'} - \frac{2}{3!}\left(\frac{m}{t'}\right)^3 + \cdots$

$t' = 1 - \frac{1}{3}\left(\frac{m}{t'}\right)^2$

~~$m = \left[3\,\frac{t'-1}{t'}\right]^{1/2} = \sqrt{\frac{3t}{t+1}} \approx \sqrt{3t}$~~ $\sim t^{1/2}$ not at all like 1/8, nor 0.32

$m = \left[3(1-t')t'^2\right]^{1/2} = \left[3|t|\underbrace{(t+1)^2}_{\approx 1}\right]^{1/2} \sim t^{1/2}$ (note: MFT ind. of dimension – becomes exact for high enough dim, often 4,) always ∞

Why are Landau theory & MFT equivalent, and why both wrong?
They ignore spatial fluctuations.

General approach to problems, not all of which can be solved exactly (like 1 & 2 dim Ising):

The — not unique (e.g., real space vs. momentum)

renormalization — not same as mass/charge renormalization in QED, although inspired by it

group — not group (no inverse)

ASK about configurations at T=0, T=∞

Show copies from Yeomans

Decimation: (numerical in this example)

$T < T_c$: before decimation, minority phase stretches almost across view – discuss correlation length, difference from random configuration
under RG, flows to T=0 fixed point

$T > T_c$: flows to T=∞

$T = T_c$: invariant (statistically)

Outline of an RG calc. in 1dim (ref. Yeomans)

~~Simplify~~ : ~~leave off bracketed terms~~ ~~(H=0)~~ } NO
Ah – but then we lose FM fixed point.

Original Hamiltonian $\mathcal{H} = -J\sum_i \sigma_i\sigma_{i+1} - H\sum\sigma_i - NG$ in 1 dim.

$$= \sum_i\left(-J\sigma_i\sigma_{i+1} - [H\sigma_i] - G\right)$$

Partition func. $Z = \sum_{\{\sigma\}} e^{-\beta\mathcal{H}} = \sum_{\{\sigma\}}\prod_i \exp\left[\beta\left(J\sigma_i\sigma_{i+1} + [H\sigma_i] + G\right)\right]$

$$= \sum_{\{s\}} \prod_{i\ \text{even}} \exp\left[\beta\left(J\,s_i\{s_{i-1}+s_{i+1}\} + H\{s_i+\tfrac{1}{2}s_{i-1}+\tfrac{1}{2}s_{i+1}\} + 2G\right)\right]$$

Now for the crucial step. Perform the sum for all even-numbered spins, i.e. circled spins → 1 and → −1. Renumber all the odd spins $2i+1 \to i$, so that (after some algebra)

$$Z = \sum_{\{s\}} \prod_i e^{-\beta'\mathcal{H}'}$$

$$\mathcal{H}' = -J'\sum_i s_i s_{i+1} - H'\sum_i s_i - N'G'$$

$$N' = \frac{N}{2} = \frac{N}{b}$$ "decimation" $b = 2$

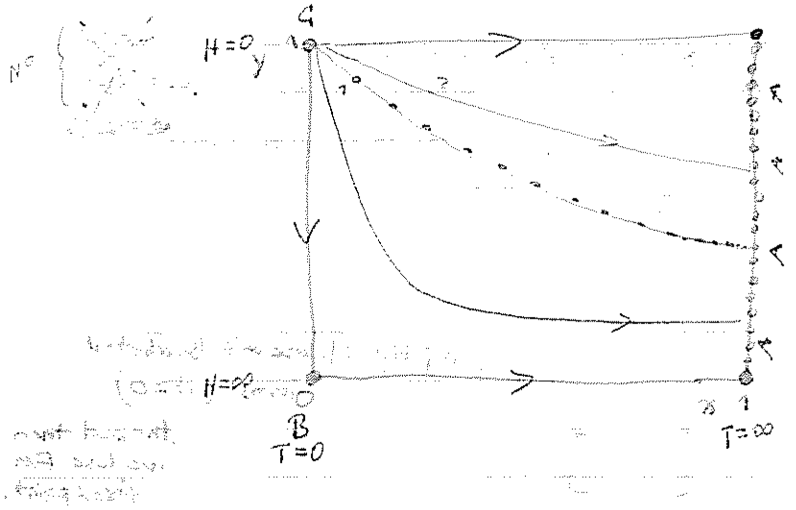
where $\overbrace{(\beta')\ J'}^{\beta' J'}$, H', C' are funcs. of J, H, C ...
(3 simult. eqns.)

G' eqn. doesn't affect spins, so skip
absorb β into J (only products βJ, βH come in)

convenient variables

$x = e^{-4\beta J}$ ← takes place of t for this 1-dim'l problem — crit temp $T_c = 0$, so t not defined

$y = e^{-2\beta H}$



Fixed points $(x', y') = (x, y)$

A) whole line $x = 1$ ($\beta = 0$ or $T = \infty$) (or $J=0$) completely disordered ($M=0$)

B) $(0,0)$: $x=0$, $y=0$
⇓ ⇓
$\beta=\infty$ $H=\infty$
$T=0$
ferromagnet

C) $(0,1)$: $T=0$, $H=0$. This is the critical point in 1dim.

If we start anywhere else, → flow under decimation [show 1].
If we let b be arbitrarily close to 1 (instead of 2), get continuous curve [show 2].

Least stable fixed point most interesting.

Since we have Z, we can get free energy per spin (recall $F = -k_B T \ln Z$).

Near $(0,1)$ fixed point, let $\epsilon = y-1$ so $(x, \epsilon)_{\text{fixed}} = (0,0)$.

Find $x' \sim 4x = b^2 x$

$\epsilon' \sim 2\epsilon = b\epsilon$

free energy $= f_0 + f_s$, f_0 smooth through transition

f_s singular

$$f_s(x,\epsilon) = \frac{1}{b} f_s(x', \epsilon') = \frac{1}{b} f_s(b^2 x, b^1 \epsilon)$$

Since unprimed has spin b times as many spins

Specific heat at or near T_c $C_v = -T_c\left(\frac{\partial^2 F}{\partial T^2}\right) \sim \left(\frac{\partial^2 f}{\partial \epsilon^2}\right)$ for a system with $T_c > 0$

Since we don't have ϵ, use x as substitute.

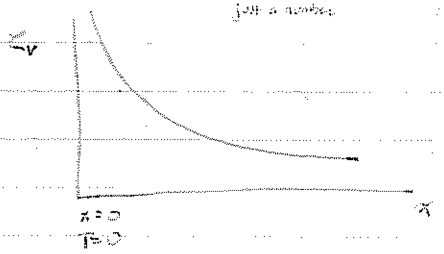
$$\frac{\partial^2 f(x,0)}{\partial x^2} \sim \frac{1}{b} b^2 b^2 f_{xx}(b^2 x, 0)$$ ~~x derivatives [illegible] nonsingular in b~~

$$f_{xx}(x,0) = b^3 f_{xx}(b^2 x, 0)$$

Forget that $b=2$, and choose it to be $x^{-1/2}$. Then

$$C_v \sim \left(\frac{\partial^2 f}{\partial x^2}\right) \approx x^{-3/2} f_{xx}(1,0) \Rightarrow \boxed{\alpha = 3/2}$$

∞ - T C_v: just a number



4/21/03 Fri: critical phenomena

today: RG

review

Review problems

Mandl 3.1 spin-1 paramagnet $(m = +1, 0, -1)$ N spins

[illegible]

$$\mathcal{H} = -\sum_i \mu B s_i$$

$$= \prod_i e^{\beta\mu B s_i^{(1)}} + \prod_i e^{\beta\mu B s_i^{(2)}} + \dots = \left[e^{\beta\mu B(-1)} + e^{\beta\mu B(0)} + e^{\beta\mu B(1)}\right]^N$$

which configuration of N spins (3^N of them)

$$Z = \sum_{\{s\}}' \prod_i e^{\beta\mu B s_i} = \left[1 + 2\cosh(\beta\mu B)\right]^N$$

magnetization $M = N\mu\langle s\rangle$; the average spin is the average of any particular spin, so

$$\langle s\rangle = \frac{1}{Z}\left(0 - 1e^{-\beta\mu B} + 1e^{+\beta\mu B}\right)\left[1 + 2\cosh(\beta\mu B)\right]^{N-1}$$

$$= \frac{2\sinh(\beta\mu B)}{1 + 2\cosh(\beta\mu B)}$$

small field or high temp: $\beta\mu B \ll 1$

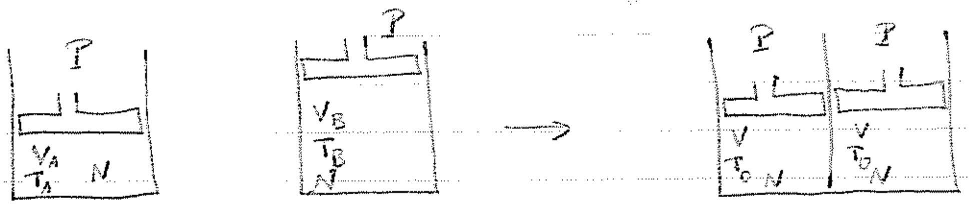
$$\langle s\rangle \approx \frac{2\beta\mu B}{3}, \quad \text{so } M = \frac{2}{3}N\mu^2\beta B$$

high field or low temp: $\beta\mu B \gg 1$

$$\langle s\rangle \approx \frac{e^{\beta\mu B}\left(1 - e^{-2\beta\mu B}\right)}{e^{\beta\mu B}\left(1 + e^{-\beta\mu B} + e^{-2\beta\mu B}\right)} \approx 1 - \underbrace{e^{-\beta\mu B}}_{\text{small}}$$

4/21/03

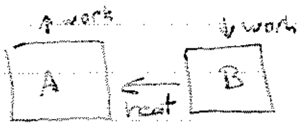
Mandl 4.2



Volumes same since P, T, N same

First, what is equilibrium temperature, T_0?

energy budget:



Energy changes (after minus before) from equipartition:

in A $\quad \Delta U_A = \frac{3}{2} N k_B (T_0 - T_A)$

in B $\quad \Delta U_B = \frac{3}{2} N k_B (T_0 - T_B)$

These parts of energy changes due to work done on each gas:

to A $\quad W_A = P(V_A - V) = N k_B (T_A - T_0)$

to B $\quad W_B = N k_B (T_B - T_0)$

The difference is heat transferred in to each gas:

$$Q_A = \frac{5}{2} N k_B (T_0 - T_A)$$
$$Q_B = \frac{5}{2} N k_B (T_0 - T_B)$$

Require $Q_A = -Q_B$: $\quad T_0 - T_A = T_B - T_0$

$$T_0 = \frac{T_A + T_B}{2}$$ just average $\qquad$ In retrospect obvious

Heat capacity of ideal gas $C_P = \frac{5}{2} N k_B$ (ind. of temp.)

$$= T \left(\frac{\partial S}{\partial T} \right)_P, \quad \text{so}$$

$$\left(\frac{\partial S}{\partial T} \right)_P = \frac{\frac{5}{2} N k_B}{T}$$

$$\Delta S = \frac{5}{2} N k_B \left[\int_{T_A}^{T_0} + \int_{T_B}^{T_0} \right] \left(\frac{1}{T}\, dT \right) = \frac{5}{2} N k_B \left(2 \ln T_0 - \ln T_A - \ln T_B \right)$$

Use T_0 = ave. temp.: $\quad \Delta S = \frac{5}{2} N k_B \ln \left[\frac{\frac{1}{4}(T_A + T_B)^2}{T_A T_B} \right]$

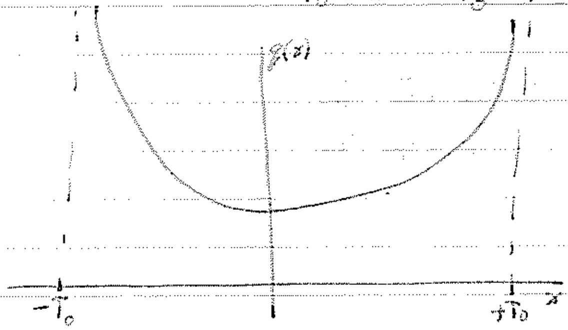
Assertion: the argument of the log is ≥ 1.

Write $T_B = T_0 + x, \quad T_A = T_0 - x$.

argument $q \equiv \dfrac{\frac{1}{4}(T_A+T_B)^2}{T_A T_B} = \dfrac{(2T_0)^2}{4(T_0-x)(T_0+x)} = \dfrac{T_0^2}{(T_0-x)(T_0+x)}$

Find extrema: $\dfrac{dq}{dx} = \dfrac{T_0^2}{(T_0-x)^2(T_0+x)} - \dfrac{T_0^2}{(T_0-x)(T_0+x)^2} = 0$

$T_0 + x = T_0 - x \Rightarrow x = 0$ only extremum!



$g(x) \to +\infty$ at $x = \pm T_0$
so $x = 0$ is a minimum.

Minimum value is $\dfrac{T_0^2}{T_0^2} = 1$

so $\Delta S \geq 0$ with equality when $x = 0$,
i.e., $T_A = T_B$.

Alternatively, we could have used Sackur-Tetrode.

Problem: Find the functional form of $P(V)$ for an adiabat of an ideal monatomic gas.

1. Sackur-Tetrode $S = Nk_B\left[\ln\left(\frac{n_Q}{n}\right) + \frac{5}{2}\right]$, $n_Q \sim T^{3/2}$, $n = N/V$

$$\Rightarrow T^{3/2} V = \text{constant}$$

i.e., for (P_1, T_1, V_1) and (P_2, T_2, V_2) two points on the adiabat,

$$\left(\frac{T_1}{T_2}\right)^{3/2}\left(\frac{V_1}{V_2}\right) = 1$$

Replace $T \to \dfrac{VP}{Nk_B}$

$$\left(\frac{P_1}{P_2}\right)^{3/2}\left(\frac{V_1}{V_2}\right)^{5/2} = 1 \Longrightarrow \left(\frac{P_1}{P_2}\right)\left(\frac{V_1}{V_2}\right)^{5/3} = 1$$

$$\text{or } P \sim V^{-5/3}$$

Alternative: $dU = TdS - PdV = -PdV$ for an adiabat; $dU = \frac{3}{2}Nk_B dT$ for ideal monatomic

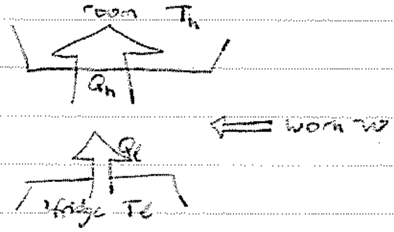
$$\frac{3}{2}Nk_B\,dT = -P\,dV = -\frac{Nk_B T}{V}dV$$

$$\frac{3}{2}\frac{dT}{T} = -\frac{dV}{V}$$

$$\frac{3}{2}\ln(T_1/T_2) = -\ln(V_1/V_2) \Rightarrow \left(\frac{T_1}{T_2}\right)^{3/2}\left(\frac{V_1}{V_2}\right) = 1 \quad \text{etc.}$$

(161)

Kittel 8.7: "to draw" refers to the motor; the heat Q_ℓ removed from the refrigerator and the heat Q_h dumped at room temp. may each be larger than the work W supplied by the motor. (All energies understood to be per unit time, so powers.)



$$\begin{cases} \frac{Q_\ell}{T_\ell} = \frac{Q_h}{T_h} \\ Q_h = Q_\ell + W \end{cases}$$

$$W = Q_h - Q_\ell = \frac{Q_\ell \, (T_h - T_\ell)}{T_\ell}$$

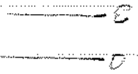
. If $T_\ell > T_h/2$, as it would typically be for a household refrigerator, $W < Q_\ell$. We can cool from T_h to $\frac{1}{2}T_h$.

4/23 4/26/04
4/25

7.14 N Bosons, spin 0

Good problem to distinguish single-particle from many-body energies.

Single-particle levels



Each can be occupied by any number of particles, so any many-body energy integer × ε is possible. We also see that chem. pot'l. is important to control N.

$$f_{BE}(0) = \frac{1}{\lambda^{-1} - 1} \quad , \quad \lambda = e^{\mu\beta} \text{ fugacity}$$

$$f_{BE}(\varepsilon) = \frac{1}{e^{\varepsilon\beta}\lambda^{-1} - 1}$$

We want $\frac{f_{BE}(0)}{f_{BE}(\varepsilon)} = 2 = \frac{e^{\varepsilon\beta}\lambda^{-1} - 1}{\lambda^{-1} - 1}$.

At the same time, μ is fixed by $f_{BE}(0) + f_{BE}(\varepsilon) = N$

two eqns. in 2 unks. (λ and β):

$$\begin{cases} f_{BE}(0) - 2 f_{BE}(\varepsilon) = 0 \\ f_{BE}(0) + f_{BE}(\varepsilon) = N \end{cases}$$

Eliminate $f_{BE}(\varepsilon)$:

$$3 f_{BE}(0) = 2N$$
$$\parallel$$
$$\frac{3}{\lambda^{-1}-1}$$

$$\lambda^{-1} = 1 + \frac{3}{2N}$$. Plug in to ratio,

so $$2 = \frac{e^{\varepsilon\beta}\left(1+\frac{3}{2N}\right)-1}{1+\frac{3}{2N}-1} = \frac{2}{3}N\left[e^{\varepsilon\beta}-1\right]+e^{\varepsilon\beta}$$

$$e^{\varepsilon\beta}\underbrace{\left(\frac{2}{3}N+1\right)}_{\downarrow} - \frac{2}{3}N = 2$$

$$\left(\frac{2}{3}N+1\right) = \frac{2}{3}N\left(1+\overset{\leftarrow \text{small}}{\frac{3}{2N}}\right), \text{ so}$$

$$e^{\varepsilon\beta} \simeq 2\left(1+\frac{1}{3}N\right)\frac{3}{2N}\left(1-\frac{3}{2N}\right)$$

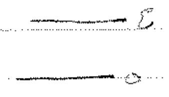
$$= \frac{3}{N}\left(\frac{1}{3}N+1-\frac{1}{2}\right)+\mathcal{O}\left(1/N^2\right)$$

$$= 3\left(\frac{1}{3}+\frac{1}{2N}\right)$$

$$= 1+\frac{3}{2N}$$

$$\varepsilon\beta = \ln\left(1+\frac{3}{2N}\right) \simeq \frac{3}{2N} \quad \text{(Taylor)}$$

$$\boxed{\tau = \frac{2}{3}N\varepsilon} + \mathcal{O}(1)\varepsilon$$



temp much larger than expected classically

Explain briefly how one might measure the temperature of an experiment near

a) 3K
b) 300K
c) 3000K.

How might such temperatures be produced and maintained?

measuring: 3K melting-curve thermometry of ^4He (coex. of solid & liq.) (need pressure cell in thermal but not diffusive contact with sample)

vapor pressure (coex. of liq. & gas)

magnetization of electronic spins in $Ce_2Mg_3(NO_3)_{12} \cdot 24H_2O$ (see K&K App. B)

speed of sound in ^3He gas (App. B)

300K Hg thermometer

ideal gas ($PV = Nk_BT$)

3000K black-body radiation
(too hot for doped sapphire fiber – melt @ 2175K)

producing: 3K pump on ^4He

300K resistive heater, cooling, etc.

3000K resistive heater (less than temp. of common tungsten incandescent bulb) in furnace

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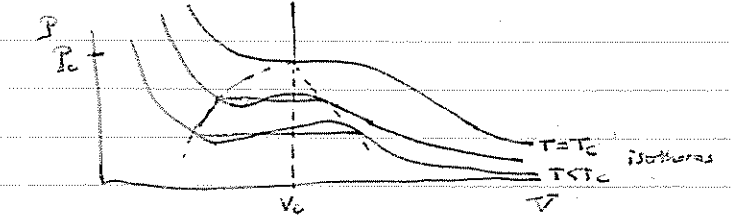
Fairly involved problem out of Thompson (4-2): C_V discontinuity in van-der-Waals fluid

(just start)

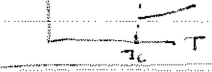
[draw better]



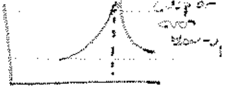
$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \quad ; \quad U_{vdw} = \frac{3}{2}Nk_BT - \frac{N^2a}{V} \qquad \text{prob. 10.1}$$

$$C_V = \frac{3}{2}Nk_B \quad \text{just as for ideal gas}$$

This is correct for $T > T_c$ but not for $T < T_c$, where we have to follow liquid and gas branches separately – neither at constant volume, even though overall volume is constant.

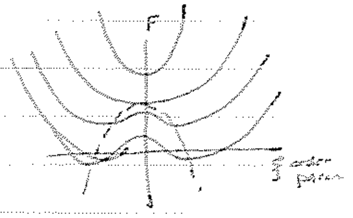


expt:



Ans: $C_V(T \to T_c^-) - C_V(T \to T_c^+) = \frac{9}{2}k_B$

Easier problem but similar: discontinuity in Landau theory
[should map on to previous]



$$F(\xi, t) = g_0(t) + \frac{1}{2}at\xi^2 + \frac{1}{4}g_4\xi^4 \qquad t = \frac{T-T_c}{T_c}$$

Get C_V from F:

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V \qquad \text{no "V" to hold constant, necessarily}$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V, \text{ so } \quad C_V = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_V = -\frac{T}{T_c^2}\left(\frac{\partial^2 F}{\partial t^2}\right)_V$$

$T>T_c$: $\xi=0$, so $F = g_0(t)$, $C_V(T_c^+) = -\frac{1}{T_c} g_0''(0)$

$T<T_c$: From notes pp152-53, $\xi^2 = \frac{-at}{g_4}$ gives minima $\pm\xi$ for $t<0$

$$F = g_0(t) - \frac{1}{2}\frac{(at)^2}{g_4} + \frac{1}{4}\frac{(at)^2}{g_4} = g_0(t) - \frac{1}{4}\frac{(at)^2}{g_4}$$

$$C_V = -\frac{1}{T_c}\left[g_0'' - \frac{a^2}{2g_4}\right]$$

discontinuity $\Delta C_V = \frac{1}{T_c}\frac{a^2}{2g_4}$

Some themes

Statistical Mechanics
- ensembles
- entropy = $k_B \ln$ (# configs.)
- temp = $\left(\frac{\partial U}{\partial S}\right)_{V,N}$
- partition function, Boltzmann factor
- quantiz'n of phase space
- Sackur-Tetrode
- kinetic theory
- flucts. small except near 2nd order crit. pt.

Thermodynamics
1. $dU = đQ + đW$
2. $dS \geq 0$
3. $\frac{S}{N} \to 0$ as $T \to 0$, $N \to \infty$ (usually)
- engines
- thermodynamic def'n of temp.
- potentials (F, G, H, etc.)
- partial derivs.

Quantum madness
- degen. Fermi gas: e.g., metal $T_F \sim 10^4 - 10^5 K$
  - few states participate in C_V at room temp
- degen. Bose gas: macroscopic gndstate occup'n even if $T \gg$ gap
  - superfluidity